

FINAL REPORT

**A Design Study Program of a
Polarographic Oxygen Analyzer for
Obtaining Data on the Atmospheric
Composition of Mars**

Period covered: 16 May 1962 to 15 September 1962

Contract No. 950284

N65-18098

FACILITY FORM 602

(ACCESSION NUMBER)

121

(PAGES)

CR-57085

(NASA CR OR TMX OR AD NUMBER)

(THRU)

(CODE)

(CATEGORY)

Prepared for

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
4800 Oak Grove Drive
Pasadena, California

MELPAR INC

A SUBSIDIARY OF WESTINGHOUSE AIR BRAKE COMPANY

3000 ARLINGTON BOULEVARD

FALLS CHURCH, VIRGINIA

GPO PRICE \$ _____

OTS PRICE(S) \$ _____

Hard copy (HC) \$ 2.00

Microfiche (MF) \$ 1.00

Final Report

A Design Study Program
of a Polarographic Oxygen Analyzer
for obtaining data on the Atmospheric
Composition of Mars

Period Covered

16 May 1962 to 15 September 1962

Prepared by

R. T. Foley
G. Halpert

Contract No. 950284

This work was performed for the Jet Propulsion Laboratory,
California Institute of Technology, sponsored by the
National Aeronautics and Space Administration under
Contract NAS7-100.

By

Melpar, Incorporated
3000 Arlington Blvd.
Falls Church, Virginia

TABLE OF CONTENTS

	<u>Page</u>
1. INTRODUCTION	6
2. SUMMARY	8
3. PRINCIPLE OF GAS PHASE POLAROGRAPHY	10
4. LITERATURE SURVEY	13
5. EXPERIMENTAL	17
5.1 Description of Cell	17
5.2 Membrane Study	21
5.2.1 Required Parameters	21
5.2.2 Types Tested	21
5.3 The Cathode (The Polarized Electrode)	37
5.3.1 Required Parameters	37
5.3.2 Types Tested and Results	37
5.4 The Anode	38
5.4.1 Required Parameters	38
5.4.2 Types Tested and Results	38
5.5 Electrolyte	39
5.5.1 Required Parameters	39
5.5.2 Types Tested and Results	40
5.6 The Laboratory Model Cell	41
5.6.1 Parts	41
5.6.2 To Assemble Cell	43

TABLE OF CONTENTS (Continued)

	<u>Page</u>
5.7 Test Procedures	45
5.7.1 Flow Systems	45
5.7.2 Electrical Instrumentation	51
5.8 Parameters and Results	53
5.8.1 Temperature	53
5.8.2 Pressure	54
5.8.3 Sensitivity	56
5.8.4 Response	56
5.8.5 Interferences	58
6. BREADBOARD DESIGN	65
6.1 Cell	65
6.2 Amplifier	66
6.3 Mechanical Development of a Breadboard Model	73
7. PROPOSED FUTURE EFFORT	91
7.1 The Electrochemical Cell	91
7.2 Amplifier and Power Supply	92
7.3 Projected Modification to Develop a Sophisticated Breadboard and Prototype	95
8. APPENDIX	99
9. BIBLIOGRAPHY	103
10. CONTRIBUTORS TO THE PROJECT	108
11. PROGRAM SCHEDULE	109

LIST OF ILLUSTRATIONS

<u>Figure</u>		<u>Page</u>
1	Typical Polarographic Wave	11
2	H-Type Polarographic Cell	19
3	Laboratory Model Cell	20
4	Membrane Testing	23
5	Early Sensitivity Measurements	36
6	Temperature Polarographs	42
7	Atmospheric Flow System	46
8	Atmospheric Flow System Schematic	47
9	Vacuum-Flow System	48
10	Vacuum-Flow System Schematic	49
11	Bridge Circuit for Current Measurements	52
12	Oxygen Pressure Sensitivity	55
13	Oxygen Concentration Sensitivity	56
14	Ozone Flow System	59
15	Ozone Flow System Schematic	60
16	Ozone Sensitivity Results	63
17	Circuit Diagram Triode Fire Stage	69
18	Circuit Diagram Pentode First Stage	70
19	Breadboard Amplifier Design	72
20	Breadboard Mockup	74
21	Air Sampling Unit	75
22	Breadboard Polarographic Cell	77
23	Breadboard Polarographic Cell	78

LIST OF ILLUSTRATIONS (Continued)

<u>Figure</u>		<u>Page</u>
24	Cell--Exploded View	79
25	Cell--Exploded View	80
26	Electrolyte Delivery Tube	82
27	Electrolyte Injector	83
28	Valve	85
29	Accumulator	88
30	Venturi Pump	90
31	Breadboard Amplifier and Regulator	93
32	Proposed Compact Design	96
33	Circuit Analysis	101
34	Program Schedule	110

1. INTRODUCTION

This is the Final Report submitted in compliance with Contract 950284 (NASA Subcontract NAS 7-100).

The objective of this contract was to conduct a design study program of a Polarographic Oxygen Analyzer for obtaining data on the atmospheric composition of Mars. The requirements were specified in JPL Statement of Work SW-2717 dated 21 November 1961, and were to include studies of the following:

- a. Sensitivity to extremely low partial pressures of oxygen.
- b. Large range of measurement capability.
- c. Reliability.
- d. Ability to withstand the sterilization temperature (145°C) for 24 hours.
- e. Establishment of operating ranges of flow rates, operating temperatures and pressures.
- f. Use of nonmagnetic materials in construction.
- g. Size, weight and power requirements.

More specifically, it was required to construct a laboratory model of an oxygen analyzer and evaluate its behavior in the following terms:

- a. At 10-100 mm Hg pressure.
- b. For effects of interfering gases (especially ozone).
- c. After being subjected to the 145°C temperature for 24 hours.
- d. Capability of redesign to the following specifications:
weight - not more than 3 lbs
volume - not more than 500 cc
power utilization - not greater than 0.5 watt

These studies are described in this report. The work on this project was actually carried beyond the contract requirements. A bread-board model of an analyzer was designed and built. An amplifier was also built and designs of a prototype along with pumping arrangements, etc., were developed.

2. SUMMARY

The contract work was initiated on the basis of known principles of gas phase polarography and a cell that had been constructed from these principles. The four main parts of the unit were studied, both individually and together, under the various conditions specified in the contract. The four parts of the cell investigated were:

- a. The membrane.
- b. The polarized electrode.
- c. The reference* electrode.
- d. The electrolyte.

After a concentrated investigation of many commercially available membranes, the membrane selected was 0.5 mil Teflon. The platinum electrode used originally as the polarized electrode was retained. The reference (reversible) electrode which proved to be most desirable was the silver-silver chloride electrode. The electrolyte, which was designed principally to conduct effectively at the lower temperatures, was found to be an aqueous methanol-potassium chloride solution. The assembly originally used was a familiar H-type cell. This was subsequently altered to provide a configuration which could be packaged into a compact unit. First a single leg of the H-cell was utilized; then a single compartment cell was constructed. The laboratory model cell with the parts described above and improved by the investigation were then subjected to the atmospheric conditions expected to be encountered during a Mars descent.

The following are the conditions chosen (with the cooperation of

* The "reference" electrode in the cell is actually a nonpolarizing reversible electrode so that the current output is a measure of the electrode reactions occurring at the polarized electrode.

the Jet Propulsion Laboratory cognizant scientists and engineers) for operation of the cell, and under which the cell operated without difficulty:

- a. Oxygen concentrations between 0.1% and 0.001%.
- b. Temperatures from 30°C to -25°C.
- c. Pressures of less than 1 mm of mercury to 760 mm of mercury (absolute).
- d. Contaminants of CO₂, NO, Ar, and O₃.

Going beyond the scope of the contract, a breadboard model of the improved polarographic instrument was designed and constructed. The major parts of the instrument are: (1) the polarographic cell, (2) the electrolyte injector and the accumulator, which allows the cell to be activated upon arrival at the planet, and (3) the amplifier, which converts current output to a voltage for transmittance.

The cell has been checked and appears to be working satisfactorily. It has not been subjected to rigorous, extended tests but no difficulty is expected. The electrolyte injector and accumulator are mockup versions of the breadboard model. For the most part, they are working pieces but have not been checked. The amplifier is capable of working over the range for which the breadboard cell has been checked.

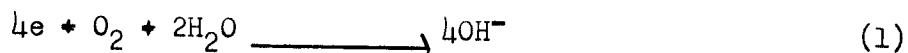
The laboratory model cell and parts, the breadboard version of the cell, the amplifier, and the mockup of the electrolyte injector and accumulator are being supplied with this report.

3. PRINCIPLE OF GAS PHASE POLAROGRAPHY

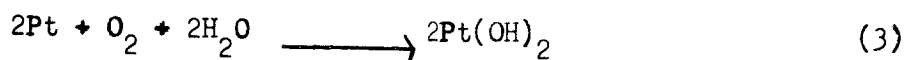
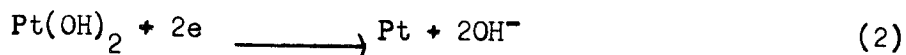
Polarography, originated in 1920 by Heyrovsky in Czechoslovakia is based on the current-potential curves exhibited by various species at microelectrodes. Oxygen is one such specie which, upon reduction, exhibits a particular polarographic wave. A typical polarographic wave appears in figure 1. This curve was obtained during the membrane study for this project, described below. The halfwave potential (designated as $E_{1/2}$) is indicated as 0.14V and is characteristic of oxygen. Above -0.3V, as the voltage is increased (in the negative direction) the current remains relatively constant. This current is called the diffusion limited current (I_d) and, in figure 1, is 15.05 microamperes.

It is the existence of this diffusion current which allows a quantitative measurement of the oxygen, because the diffusion current of the oxygen is related in a linear fashion to the concentration gradient of oxygen diffusing to the electrode surface. If it is assumed that oxygen reduction takes place immediately upon arrival at the electrode surface, i.e. the concentration of oxygen at the electrode surface is zero, then the diffusion current is directly proportional to the concentration of oxygen in solution (or in the outer gas phase).

The reduction of oxygen has been generally assumed to proceed by the following reaction.



However, more recent investigation²⁸ has led to the following mechanism at platinum microelectrodes:



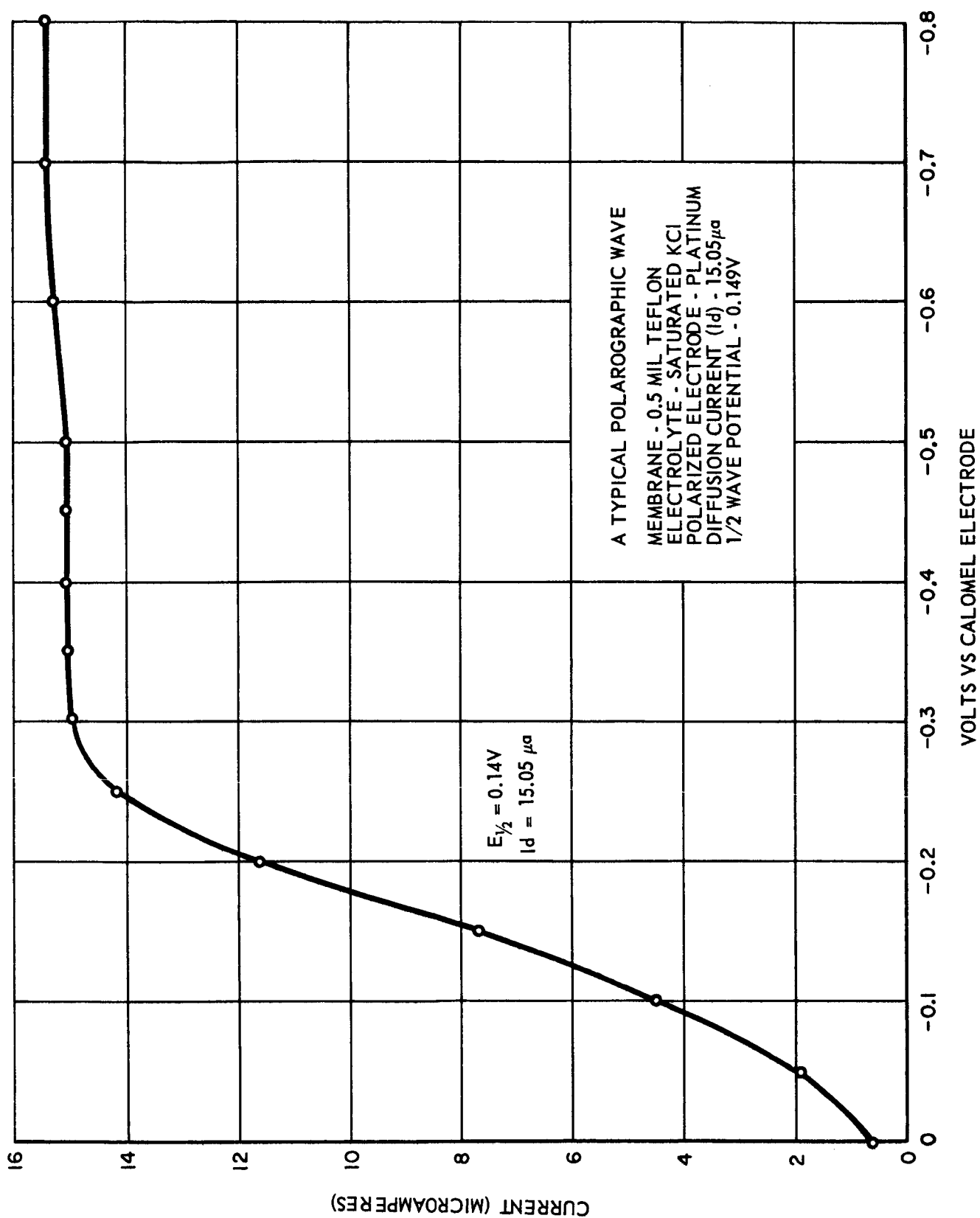


Figure 1. Typical Polarographic Wave

Reaction (2) is the reduction of the oxide film present and reaction (3) the oxidation of the platinum electrode to the oxide by oxygen. Reaction (1) has been found to occur directly after specialized pretreatment of the platinum electrode but has been found to be pH sensitive.

The reduction of oxygen in solution is widely observed in polarography as an interference. A recent innovation has been the polarographic determination of gases by diffusion through permeable membranes. Oxygen has been found to exhibit a high rate of diffusion through certain membranes and thus can be quantitatively detected by the measurement of a diffusion current occurring from a platinum electrode which is also in contact with the gas mixture containing oxygen.

4. LITERATURE SURVEY

Before experimental work was initiated a considerable amount of reference work was completed on the various subjects involved in the design and operation of a gas polarographic analyzer. Among the areas of interest were: diffusion, membranes, polarography, other oxygen detectors, contaminants, amplifiers, and atmosphere compositions of Mars.

Since it was not feasible to devote time to the detailed study of absolute diffusion or permeability measurements in the laboratory, reasonable time was spent investigating the literature for applicable information.

Two general references on diffusion^{1,2} discuss the principles of diffusion although neither covers, directly, the subject of diffusion through membranes. A standard method for measurement of gas transmission rates was developed by the Dow Chemical Company and was made an ASTM standard³. The original reference to this method is discussed by Brown and Sauber⁵. They measured oxygen, nitrogen, and carbon dioxide gas transmission rates. Barton⁴, in Great Britian, determined permeability to hydrogen and argon as well as the above. A final report⁶ on a Quarter-master R and D contract DA 19-129 QM 123 by Stannet, Szwarch, and Myers of the College of Forestry, State University of New York, included permeability studies of oxygen, nitrogen, carbon dioxide, hydrogen sulfide, and water vapor, as well as factors affecting permeability such as crystallization and irradiation. Kammermeyer⁷ investigated the permeability of silicone rubber. References 8 through 18 were of similar treatments utilizing various methods to determine permeability and diffusion rates. Since various methods were utilized in determining these rates, a variety

of units of measure were derived and it was found that they were not all interchangeable. Smirl and Hershberger¹⁹ also studied permeability to organic vapors.

The design of ozone generating equipment and the experimental use thereof is covered in Ozone Chemistry and Technology⁴⁵, ACS Advances in Chemistry, Series No. 21. For further information, a bibliography on ozone⁴⁶ is also available.

The study of Polarography is covered very well in Kolthoff and Lingane's volumes.⁴⁸ The oxygen section (pages 552-228) is particularly valuable. Brezina and Zumansbook which is a translation from the Czech "Polarography in Medicine, Biochemistry and Pharmacy"⁴⁹ (pages 136-161) is also especially informative and discusses the use of absolute alcohols as solvents and calcium chloride as a supporting electrolyte and drying agent. Reimouth²⁰ and Delahay⁵⁰ offer excellent discussions of electrochemical processes and instrumentation.

The electrochemical behavior of the platinum microelectrode is discussed at length^{22,23} in two of the earliest complete studies on the use of the platinum electrode in voltammetry (the determination and interpretation of current-voltage curves). Lingane²⁴, Anson²⁵, Lingane and Anson²⁶ and Kolthoff and Tanaka²⁷, have studied the use of platinum in electrolysis and discuss the treatment of electrodes as well as the mechanism. In Kolthoff and Tanaka's paper²⁷, the effects of rotating vs. stationary electrodes are included. Laitinen and Enke²⁸ have discussed the dissolution of oxide films on platinum and have included mechanisms of formation and evolution of oxygen. Interferences of peroxide in the determination of oxygen is discussed by Kolthoff and Jordon⁵¹.

The discussion of the reduction of oxygen in solution at various microelectrodes, discussed by Sawyer and Interrante²⁹, serves as an excellent reference in that it pertains to the subject directly. In addition to platinum, the discussion includes palladium, nickel, lead, zinc, cadmium, copper, and tungsten. Bagotski and Motov³⁰ reported on the study of reduction of oxygen in basic solutions.

A number of electrochemical methods and instruments have been used in the analysis of oxygen. Some of these are discussed in the literature. (See references 31, 32, 36 through 41, and 52.). The description of the gas polarographic principal is elucidated in the paper by Sawyer, George, and Rhodes³⁵. An oxygen electrode used in biological systems has been described by Orritt and Kanwisher³⁴, and Rayment³³ measured the effect of temperature on this instrument. This cell contained a potassium chloride electrolyte. The purification and use of acetonitrile as a solvent in electrochemical processes was discussed in another reference⁴².

Shilling⁴³, in his publication, for the Rand Company, on the atmosphere of Mars, gives insight to the temperature, pressure, and concentrations of oxygen and ozone to be expected. Kellogg and Sagan⁴⁴ also offer a predicted atmospheric composition of Mars as well as Venus. Miller⁴⁷ discusses some of the instrumentation evolved for Mariner probes.

Existing electrometers suitable for this type of application were few in number. Praglin and Nichols⁵⁸ gave an approach using electron tubes at the input. Beneteau⁵⁹ designed an unusual differential amplifier eliminating much h_{fe} variation found in the previous slaughter circuits⁶³. Zeroing and stabilization methods for DC amplifiers were proposed both by Goldberg⁶⁵ and Williams et al.⁶⁴

AC amplifier principles were discussed by Ludwig⁶¹ and a Melpar chopper was found compatible in conjunction with this type of amplifier system.

Field effects for the first stage of amplification were considered⁵⁵ and numerous personal contacts were made in connection with this area, since time has not been sufficient to allow many publications of this method. Personal contacts have been made with Crystalloines, Texas Instruments, Fairchild Semiconductor, Ameleo Inc., Naval Research Laboratory, Page Engineering, Goddard Space Flight Center, and the Space Physics Laboratory, State University of Iowa.

Individual electronic components reliability was investigated through the JPL specification No. 20061, the vendors, and Melpar's Minuteman program, (unclassified report No. 14). Holladay⁵⁷ discussed failure prediction by observation of characteristics curves. A Wescon report⁵³ discussed the problem of neutron damage in Mesa transistors. Personal contact of D. M. Brown, Goddard Space Flight Center, resulted in a valuable analysis of temporary radiation damage in gas-filled PNP silicon Mesa and Planar type transistors being made available.

Power Supplies were investigated⁶⁰, and gave a straight forward design analysis.

5. EXPERIMENTAL

This section describes the experimental work leading to the design and construction of a laboratory model cell which would work satisfactorily under the specified conditions. In this phase of the program, size, weight, and power requirements were of concern only in so far as the final specifications for these parameters could be predicted and were within the required limits. A general description of the polarographic cell will be followed by a more comprehensive discussion of the cell parts.

5.1 Description of the Cell

The principle of gas-phase polarography was investigated, a crude laboratory model was constructed, and experimentation was accomplished with the apparatus to prove that the principle worked.

In making a polarographic measurement, a cell is required which must contain an electrode to be polarized, a second reversible, nonpolarizing electrode, and an electrolyte. A power supply must be available to apply a potential over a given range and a galvanometer must be in the circuit to determine the current flowing at the applied potentials. Various instruments are available commercially as polarographs which are self-contained units.

The cell used on initiation of this program was an H-type cell. The polarized electrode utilized was a platinum inlay electrode, situated in one leg of the cell; the reversible electrode was a calomel type situated in the other leg. A fritted disc and an agar plug separated the two compart-

ments. The electrolyte was an aqueous saturated potassium chloride solution. A preliminary polarization curve was run with oxygen passing through the chamber containing the platinum electrode. This was accomplished by varying the voltage between the two electrodes and noting the current. The current was level and found to be independent of voltage between -0.3v and -0.7v vs. the calomel electrode. This was a definite indication that the diffusion of oxygen in solution to the surface of the platinum electrode was the current limiting factor.

The bottom of the polarization chamber was cut off, and, in its place, a polyethylene membrane was sealed. The platinum inlay electrode was taut against the membrane such that it would be directly in the line of flow of the oxygen diffusing through the membrane as seen in figure 2. The polarization curve was again run, and the results (figure 1) were similar to those of the polarization of oxygen in solution.

It now remained to study the effects of each component and to optimize the system so that it would operate within the required specifications.

Midway in the program a design change was initiated. It was thought that, for simplicity, the silver-silver chloride wire could be placed in the same chamber as the platinum electrode. This was done with the silver-silver chloride electrode spiraled around the platinum (see figure 3). The cell worked as well as the H-type cell. The new single-channel configuration could be easily designed to the specifications required, and thus it was designated during the rest of the project as the laboratory model cell.

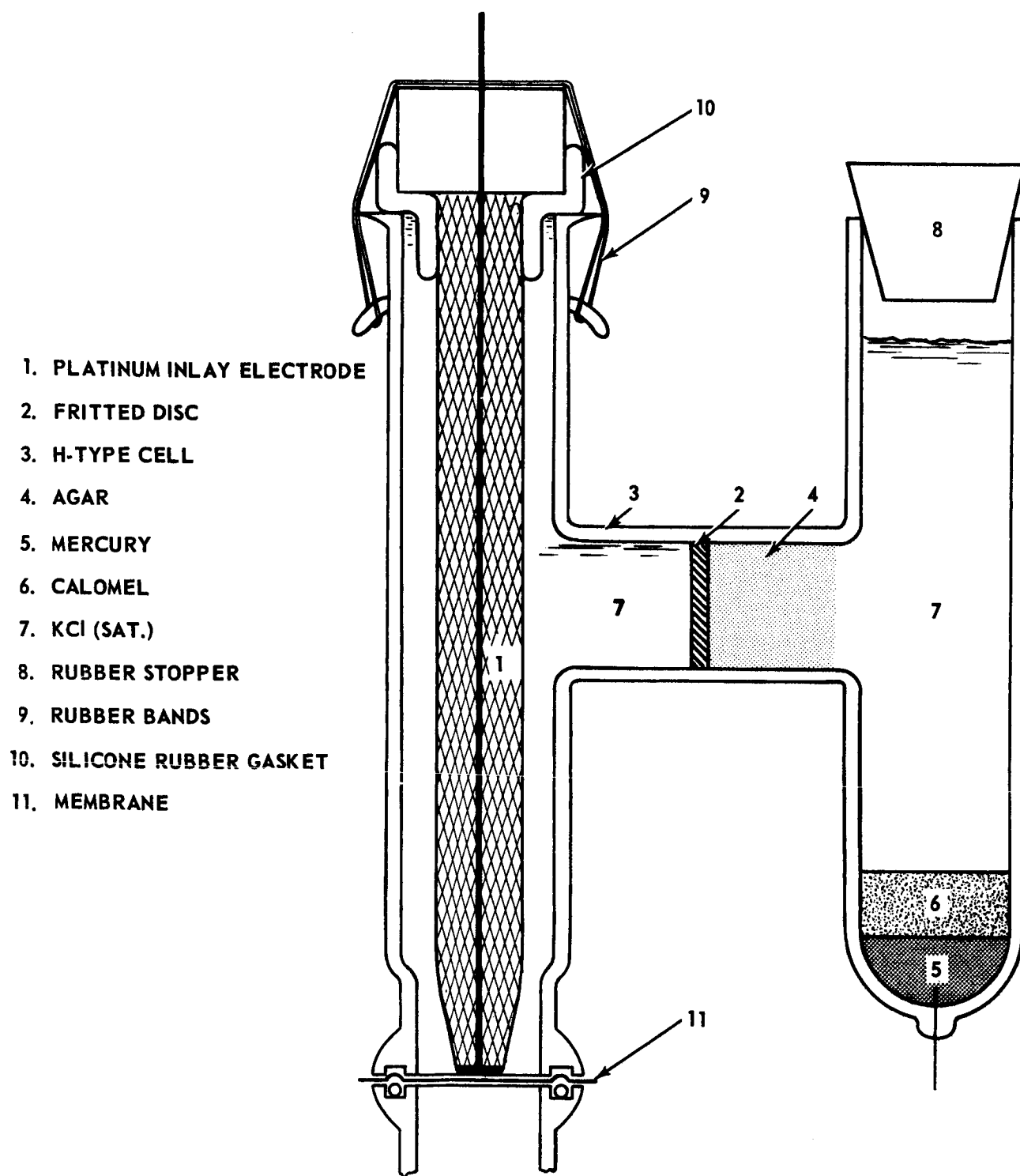


Figure 2. H-Type Polarographic Cell

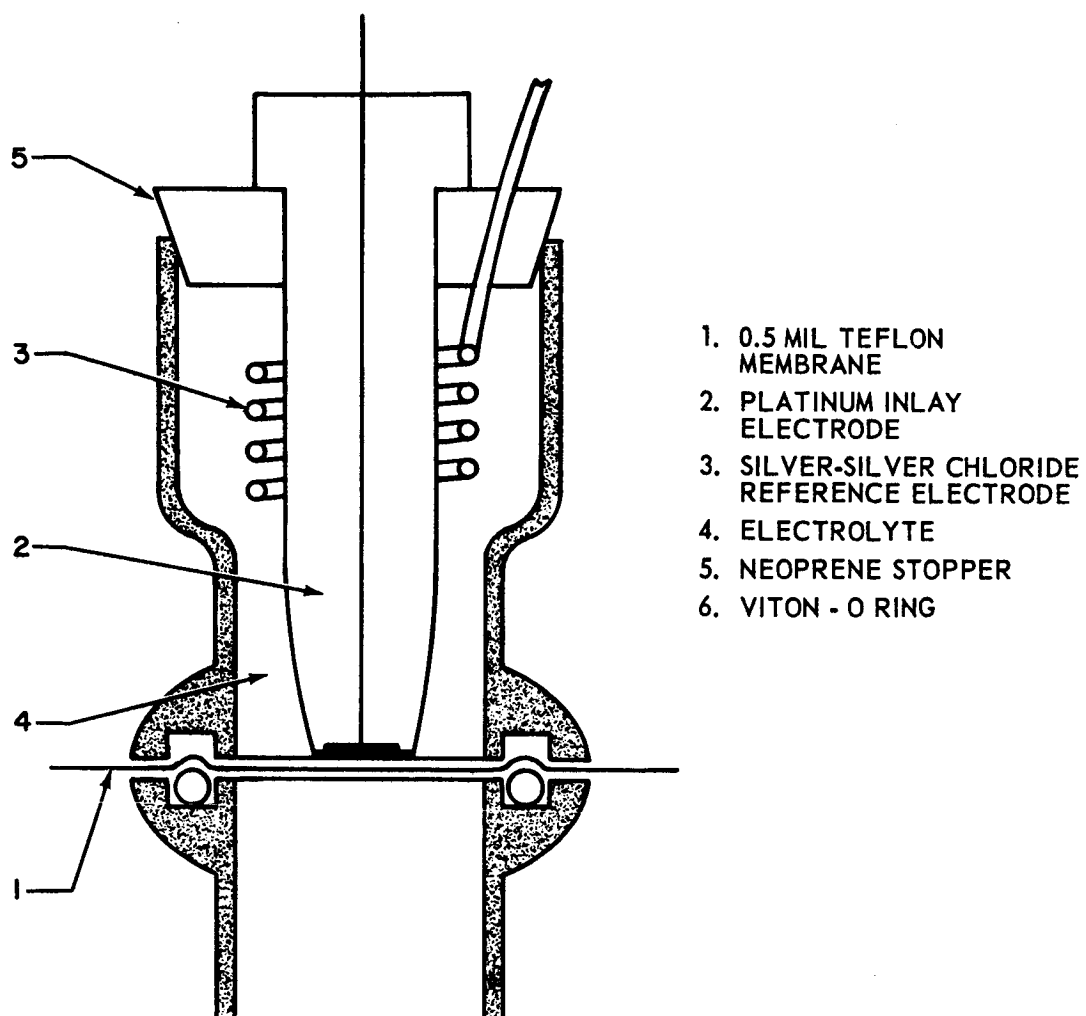


Figure 3. Laboratory Model Cell

5.2 Membrane Study

5.2.1 Required Parameters

The membrane is a component very critical to the working of the polarographic oxygen detector. It is the only part of the entire instrument that is itself subjected directly to the environmental conditions of the Martian atmosphere. It must withstand not only the sterilization temperature of 145°C for 24 hours, but, also, must retain the same oxygen permeability characteristics after the sterilization. It must not be altered in any way by radiation. In the Martian atmosphere it must be capable of working within a temperature limitation of -20°C to +20°C, and at pressures of 10 mm Hg to 100 mm Hg without breaking, tearing, or excessive stretching. It must be capable of diffusing oxygen over the range of pressures equivalent to oxygen contents of 0.001 to 1 percent.

The peculiar property required of the membrane was that it retain the electrolyte on one side under certain required conditions while the other side of the membrane was exposed to the atmosphere. Thus, the membrane had to be permeable to oxygen and yet not so porous that the electrolyte would leak out. The distinction between permeability and porosity is a fine one because it is difficult to determine where one begins and the other ends. In the testing this did become obvious.

5.2.2 Types Tested

The plan was to first sort out from the great number of available membrane materials those that had the characteristic of high oxygen permeability. In all, more than 60 membranes were tested with a total of

150 polarographic tracings being made. Figure 4 is a photograph of the apparatus used in the membrane testing. It consists of the H-type cell in which the membranes were changed from one run to another, a platinum inlay electrode, and the Electrode which was used to apply voltage and to give a current measurement. From the literature and from previous experimental work polyethylene was known to be a suitable membrane for oxygen diffusion. Work was initiated using polyethylene membranes. The diffusion currents were measured for membrane thicknesses of 6 mils to 1 mil. As expected, the 1-mil membrane allowed a higher oxygen diffusion rate. The work with polyethylene is tabulated in table 1. As can be seen, the experimental results with polyethylene were rather reproducible and served as a reference during the early stages of membrane testing. During this time, the operation of pressing the platinum electrode against the membrane was found to be nonreproducible. The degree of stretching of the membrane resulted in slight variations in the measured diffusion current. The actual thickness of the membrane was found to vary, and this also was reflected in the diffusion current. Dupont was the main source of polyethylene film, but Dow's polyfilm and Visking's polyethene were also tested. The polyethylene membranes were all of the low-density type.

The next material to be found to have the characteristic of high-oxygen permeability was Teflon. This was expected from an examination of the literature.

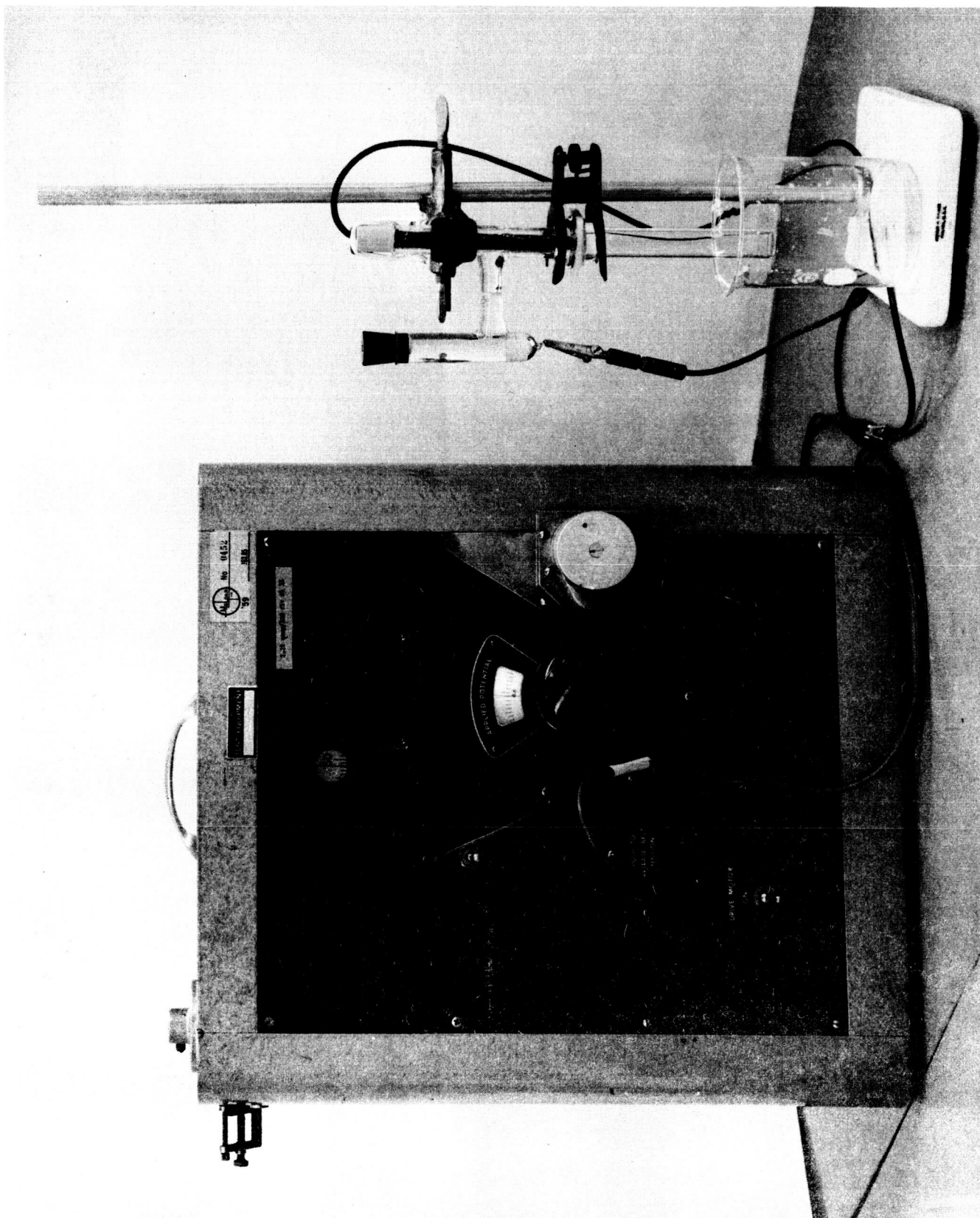


Figure 4. Membrane Testing

TABLE I
Membrane Testing — Polyethylene^{ab}

Graph Number	Manufacturer	Thickness (mils)	Diffusion Current (μ a)	Halfwave Potential (volts)
6-01	DuPont	1	6.44	0.23
6-02	DuPont	1	9.10	0.28
6-03	DuPont	1	7.66	0.25
6-04	DuPont	1	10.43	0.29
6-05	DuPont	1	7.77	0.23
6-05-1	DuPont	1	7.77	0.24
6-05-2	DuPont	1	9.21	0.31
6-05-3	DuPont	1	7.10	0.22
6-06	DuPont	1	8.77	0.28
6-06-1	DuPont	1	8.88	0.28
6-06-2	DuPont	1	8.88	0.22
6-06-3	DuPont	1	6.55	0.21
6-07	DuPont	2	5.99	0.35
6-08	DuPont	2	5.35	0.31
6-17	DuPont	1	9.3	0.33
6-20	DuPont	1	4.66	0.18
6-21	DuPont	1	9.77	0.28
6-22	DuPont	1	9.88	c
6-27	DuPont	1	9.37	0.35
6-28	DuPont	1	9.55	0.30
6-66	Dow (Polyfilm)	4	1.67	c

TABLE I (Continued)

Membrane Testing — Polyethylene^{ab}

Graph Number	Manufacturer	Thickness (mils)	Diffusion Current (μ a)	Halfwave Potential (volts)
6-67	Dow (Polyfilm)	6	1.12	c
6-68	Visking (Polythene)	1	5.13	0.28
6-72	Visking (Polythene)	1.5	2.12	c

-
- a. Tests Made in H-type Cell - Polarized Electrode - Platinum Inlay
Reference Electrode - Saturated Calomel
Electrolyte - Saturated KCl
Measurements made with Fisher Elecdropode.
- b. Results of Temperature Tests - All polyethylene membranes melted when subjected to 145°C for 24 hours.
- c. Not determined.

The data accumulated during the Teflon testing are given in table II. As can be noted, the diffusion currents for the 1-mil Teflon were similar to those of the 1-mil polyethylene membranes. However, it was found that a 0.5-mil Teflon membrane was available from duPont. This membrane exhibited a different stretching property than polyethylene. Although an attempt was made to reproduce the platinum pressure on the membrane each time, a wider variation in diffusion current resulted. However, it was obvious that the 0.5-mil Teflon exhibited an I_d that was at least two times greater than the polyethylene. As the testing with Teflon progressed, more and more reproducibility was established, and, as seen in table II, six tests in the last eight were within 1 μ a. This can be explained as being due to the variation of membrane thickness and nonreproducible stretching.

Silicon rubber was a membrane that was expected (from the literature) to be the best and it at first appeared entirely acceptable, but later it was found to vary widely (see table III.). The very first run (6-25) with the 52.1-microampere diffusion current was never reproduced. The membrane was a 10-mil-thick silicone rubber, and, for this reason, also appeared to be more desirable (greater strength, etc.). Even when a 5-mil silicone rubber sheet was made available, the results were found to be unsatisfactory. Some hope was given to the ultimate use of this material in the last two runs where results were very similar. It is expected that a thinner membrane may be more useful; however, the problem of strength would be much greater in a thinner membrane.

TABLE II

Membrane Testing — Teflon^{ab}

Graph Number	Thickness (mils)	Diffusion Current (μ a)	Halfwave Potential (volts)
6-10	1	7.05	0.28
6-12	1	5.33	0.17
6-23	1	8.05	0.26
6-24	0.5	33.31	0.47
6-29	2 ^c	7.16	0.35
6-34	0.5	27.5	d
6-34-1	0.5	25.9	d
6-75	0.5	12.4	0.37
6-102	0.5	19.6	0.23
6-82	1	10.7	0.35
6-83	1	12.2	0.33
6-94	0.5	15.8	0.35
6-94-1	0.5	15	d
6-100	0.5	7.5	d
6-100-1	0.5	18.7	d
6-100-2	0.5	20.5	d
6-100-3	0.5	18.4	d
6-100-4	0.5	21.0	0.42
6-101	0.5	22.3	0.42
6-101-1	0.5	19.5	0.23

TABLE II (Continued)

Membrane Testing — Teflon^{ab}

Graph Number	Thickness (mils)	Diffusion Current (μ a)	Halfwave Potential (volts)
6-102-1	0.5	18.5	0.22
6-102-2	0.5	20.4	0.22
6-103	0.5	20.1	0.30
6-103-1	0.5	20.8	0.24
6-105	0.5	20.1	0.36
6-105-1	0.5	15.1	0.15

-
- a. All Tests Made in H-type Cell - Polarized Electrode - Platinum Inlay
Reference Electrode - Saturated Calomel
Electrolyte - Saturated KCl
Measurements Made on Fisher Elecdropode
- b. Results of Temperature Tests - Teflon Membranes all appeared to be unaffected after 24 hours at 145°C.
- c. From Polymer Corporation.
- d. Difficult to determine the halfwave potential from the data.

TABLE III
Membrane Testing — Silicone Rubber^a

Graph Number	Manufacturer	Thickness (mils)	Current (μ a)	E 1/2
6-25	Norris	10	52.10	0.385
6-28-1	Norris	10	13.32	b
6-36	Norris	10	20.87	b
6-40	Norris	10	16.70	0.255
6-95-1	Materials Testing	5	13	b
6-95-1	Materials Testing	5	16.5	b
6-104	Materials Testing	5	20.0	0.20
6-104-1	Materials Testing	5	8.25	0.173
6-104-2	Materials Testing	5	8.03	0.163

a. All tested made in H-type Cell - Polarized Electrode - Platinum Inlay
Reference Electrode - Saturated Calomel
Electrolyte - Saturated KCl
Measurements made on Fisher Elecdropode

b. Difficult to determine the halfwave potential from the data.

Many other membrane materials were tested in a similar manner. Table IV is a listing of some of those membranes. None resulted in a satisfactory diffusion current.

The difference between permeability and porosity was noted in that porous membranes, such as the Pellon types, those supplied by Radiation Applications Laboratory, and the borderline case of microporous (micron size holes) polyethylene and polyvinylchloride yielded electrolyte leaks, whereas those that were permeable to oxygen satisfied the diffusion requirement.

In the meantime, sterilization temperature tests were being made on the various membranes to determine the effects of 145°C for 24 hours. An oven was used and the temperature was maintained to within $\pm 2^\circ\text{C}$. Three check runs were made on each sample. The first two were identical in which the membranes were examined for visible effects. The last temperature test included a weight measurement before and after to determine whether any part of the membrane was destroyed. Every sample of polyethylene in both temperature runs melted as expected, and thus this material was definitely eliminated from further consideration. The silicone rubber and Teflon membranes showed no visible effects in either of the first two temperature runs. The results of the last temperature test showed an average of 0.01 percent weight loss for Teflon and an average of 1 percent weight loss for silicone rubber.

The cell was run utilizing one of the Teflon membranes that had undergone the sterilization temperature tests. The cell operated as well as if the membrane had been freshly cut.

TABLE IV
Membrane Testing -- Other Membrane^{ab}

Graph Number	Membrane	Company	Thickness (mils)	Diffusion Current (μ a)	Halfwave Potential (volts)	Overtest	Physical Characteristic
6-70	Battery Separator	Visking	3	1.12	c	Yellowed	Transparent
6-71	Battery Separator	Visking	3.5	1.6	c	Brownish-black and rolled	Translucent
6-46	Cellophane	DuPont	1	d	c	Brittle and brown	Clear
6-45	Cellulose Acetate	DuPont	1	3.12	0.21	N.V.E. ^b	Clear
6-76	Silicon Coated Glass Cloth-1010 Hard Rubber	Connecticut	7.5	d	c	N.V.E. ^b	
6-77	Silicone Coated Glass Cloth-3010 Hard Rubber	Connecticut	12.5	d	c	N.V.E. ^b	
6-78	Silicone Coated Glass Cloth-1015 Hard Rubber	Connecticut	14.5	d	c	N.V.E. ^b	
6-32	Ethafoam (Expanded Polyethylene)	Dow	1/8 (inch)	d	c	Melted into brownish-yellow	
6-33	Ethafoam (Expanded Polyethylene)	Dow	1/8 (inch)	d	c	Melted, brownish-yellow	Foam-like material
6-98	Gum Rubber	Potomac Rubber Company	10 1/2	4.55	0.30	Slightly Darkened	

TABLE IV (Continued)

Membrane Testing -- Other Membrane^{ab}

Graph Number	Membrane	Company	Thickness (mils)	Diffusion Current (μ a)	Halfwave Potential (volts)	Oventest	Physical Characteristic
6-48	Saran Wrap	Dow	0.5			Dark Brown adhered Clear to w.g.	
6-26	Sausage Casing	Visking	2	1.72	0.36	Dark yellow	Translucent
6-27	Sausage Casing	Visking	1	3.89	0.35	Slightly yellow	Translucent
6-49	Sausage Casing	Visking	3	1.67	c	Medium brown stuck slightly to w.g.	Translucent
6-50	Sausage Casing	Visking	1.5	3.35	0.28	Yellowed	Translucent
6-42	"Scotch Pak"	3M Co.	4.5	d	c	Slightly yellowed adhered to w.g.	Clear
6-84	Silicone Rubber	RTV-11 G.E.	12 (app.)	d	c		
6-57	S.F.P. H-85	Pellon	4	d	c		Membrane too porous to hold KCl
6-58	S.F.P. H-92	Pellon	5	d	c		Membrane too porous to hold KCl
6-61	S.F.P. H-133	Pellon	2	d	c		Membrane too porous to hold KCl

TABLE IV (Continued)
Membrane Testing -- Other Membrane^{ab}

Graph Number	Membrane	Company	Thickness (mils)	Diffusion Current (μ a)	Halfwave Potential (volts)	Oventest	Physical Characteristic
6-74	Microporous Polyethylene	Reeves	4 1/2	4.91	0.29	Brownish-yellow adhered to w.g.	
6-79	Microporous Polyvinyl Chloride	ESB Reeves Co.	10	9.92	c	Turned very light brown	
6-87	Moleskin Tape	Arno Adhesive Tapes, Inc.	40	d	c		Black cotton
6-47	Mylar	DuPont	0.25	0.78	c	N.V.F. ^b	Clear
6-99	Neoprene	Potomac Rubber	15.5	0.40	c	N.V.F. ^b	Black Color
6-92	Nylon	Polymer	2	d	c		
6-72	Polyethylene	Visking	1.5	2.12	c	Brown and rumpled	Clear
6-66	Polyfilm	Dow	4	1.67	c	Melted	Black in color
6-67	Polyfilm	Dow	6	1.12	c	Membrane melted and yellowed	Clear
6-90	Visqueen	Visking	0.75	7.14	0.37	Melted into a brownish-yellow film	Translucent

TABLE IV (Continued)

Membrane Testing -- Other Membrane^{ab}

Graph Number	Membrane	Company	Thickness (mils)	Diffusion Current (μ a)	Halfwave Potential (volts)	Oventest	Physical Characteristic
6-91	Visqueen	Visking	1	5.91	0.35	Melted into a brownish yellow film	
6-44	Tedlar	DuPont	0.5	0.18	c	Very slightly yellowed	Clear
6-89	Trithene	Vis-Queen	5	d	c	N.V.F ^b	Clear
6-43	Trycite	Dow	2.5	3.79 4.57	0.20 0.55	Dark yellow adhered to w.g.	Clear

a. All tests made in H-type cells - Polarized Electrode - Platinum Inlay
Reference Electrode - Saturated Calomel
Electrolyte - Saturated KCl
Measurements made on Fisher Eledropode.

b. NVE refers to no visible effect.

c. Difficult to determine.

d. A diffusion current was not indicated.

Various sensitivity studies, as well as contamination studies were run utilizing the apparatus in figure 5. The crude flow system was designed to roughly test the effects of various concentrations of oxygen and contaminants on the polyethylene, Teflon, and silicone rubber membranes. The Leeds and Northrup Electrochemograph performs a similar function to the Eledropode in figure 4, and in addition has as a current readout device, a chart recorder. The H-type cell was utilized during this study also.

When all the comparative experimental work was completed on the membranes, it was concluded that a 0.5-mil-thick Teflon membrane would function well within the required specifications. Thus the tests over the last half of the program were conducted on a cell utilizing a 0.5-mil Teflon membrane. In the low pressure environments it would be necessary to back the membrane with a screen to keep it from being sucked out or from having it pulled away from the platinum electrode.

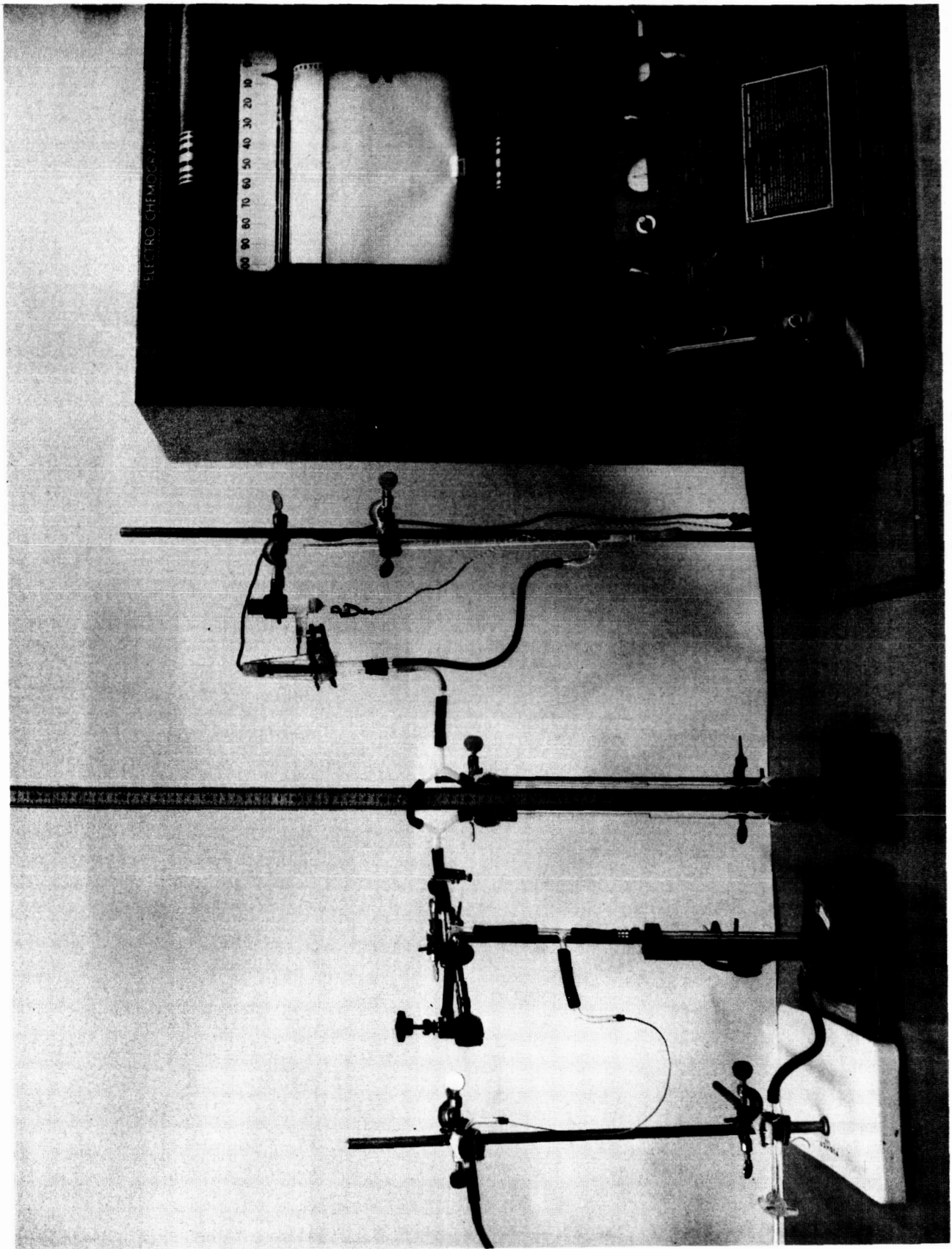


Figure 5. Early Sensitivity Measurements

5.3 The Cathode (The Polarized Electrode)

5.3.1 Required Parameters

The polarographic principle requires that only one electrode be polarized, i.e., current will flow only when the electrode reaction is initiated at that electrode. In the present case oxygen depolarizes the electrode, causing current to flow. The other electrode must be a reversible, nonpolarizing type as discussed below. Referring to figure 1, it is obvious that if the cathode is polarized negatively to 0.75 v, then current will flow by virtue of oxygen depolarization, and the current will be proportional to the oxygen concentration. The electrode must be inert at the potentials applied. It must not be affected by high and low temperatures. The surface must remain uniform so that it will be available to the oxygen diffusing through the membrane. Finally, it must not be attacked by the electrolyte.

5.3.2 Types Tested and Results

The electrode which was utilized in the original study was a platinum electrode. The particular configuration used was a platinum inlay electrode made by Beckman. It consists of a long tube through which a platinum wire passes. The wire makes perpendicular connection at the end of the tube to 3/8-inch diameter circular platinum sheet. This sheet is imbedded in the tube and then ground level with the glass. The only part of the platinum electrode exposed to the electrolyte, then, is the outside of the platinum disc. The structure of this electrode can be seen in figures 2 and 3.

Platinum is the most desirable material to use since it is inert at the reduction potentials used. Since this did work well through all the stages of progress, it was decided to utilize platinum as the cathode (polarizing electrode).

5.4 The Anode

5.4.1 Required Parameters

The anode, in the case of cathodic polarography, is required to be a reversible, nonpolarizing electrode. By that it is meant that neither the potential applied to the two electrodes nor the current drain shall alter it chemically. Its surface area should be large enough to maintain its condition of reversibility over the required time periods. If the reaction proceeding at the anode is limited in any way, there will be a polarizing effect on it and the potential at the working electrode (cathode) will be changed. The saturated calomel electrode is often used for this purpose and for a reference electrode. It is made of mercury, covered successively with a paste of mercurous chloride and mercury (calomel), and then with saturated potassium chloride solution. Thus, the mercury surface is in contact with mercurous chloride and the mercurous chloride with the potassium chloride. For the present application, the anode should be so constructed that the cell will work in any position. Further, it must be able to withstand the sterilization temperature and operate well at the lower temperatures of -20°C .

5.4.2 Types Tested and Results

The first reversible nonpolarizing anode was the saturated calomel electrode. It has been demonstrated to be perfectly adequate for polarographic

work under ordinary conditions, but the problems associated with adapting this type of electrode to the present applications would be considerable. This electrode was utilized during all of the early work involving the membrane study. One calomel electrode configuration that uses a mercury filled ceramic exists, and it could possibly have been developed for this application.

The silver-silver chloride electrode has been widely used as a reversible, nonpolarizing electrode in many electrochemical studies. In addition, it has been known to be used widely as a reference electrode in organic systems. Since it was foreseen that alcohols and glycol electrolytes might be utilized, this electrode was favored.

The silver-silver chloride electrode was made up from a silver wire. It was placed in the calomel limb of the H-cell, and the measurements of cathode vs. calomel and cathode vs. silver-silver chloride were made. It was found that there was no difference in the diffusion currents at certain applied potentials. The silver-silver chloride electrode also is known to be capable of withstanding the required temperature specifications. It has been utilized satisfactorily in the single channel cell by wrapping a spiral of the wire around the platinum inlay electrode as seen in figure 3. Thus, the silver-silver chloride electrode was accepted as the anode in the oxygen analyzer.

5.5 Electrolyte

5.5.1 Required Parameters

The electrolyte should be capable of ionic conduction at the lower temperature limits. It is necessary that it functions satisfactorily after

having been subjected to the sterilization temperatures. Also, besides being incapable of functioning with the electrodes, it should not react adversely with them.

5.5.2 Types Tested and Results

The electrolyte used in the early tests was an aqueous, saturated, potassium chloride solution. It was utilized for all of the testing work until the other three major cell parts were decided upon. The sterilization temperature presented little problem since the electrolyte will be sealed in a bellows during this high-temperature period and during the flight. However, for the low-temperature specification, saturated KCl was not desirable since its freezing point is about -12°C .

It was expected that glycol- H_2O -KCl mixtures would be ideal for this situation. However, this mixture is quite viscous. Because of this, the ion flow is retarded, and therefore the diffusion current in this case was reduced considerably.

Methanol- H_2O -KCl mixtures had a similar effect of reducing the freezing point to below the specified low-temperature requirement. A reduction in current occurred because the KCl was not very soluble in the methanol solution. The reduction in diffusion current from $22\text{ }\mu\text{a}$ to $17\text{ }\mu\text{a}$ was not objectionable, and thus it was decided that this mixture would be utilized. The mixture was prepared with a composition such that the solution would not be supersaturated at the lower temperature of -20°C . The mixture established empirically was 70 cc H_2O and 5 grams of KCl made up to 100 cc with methanol. The freezing point was determined approximately and was found to be -27°C .

One significant point that should be noted is that the halfwave potential $E_{1/2}$ was displaced by using this solution and that the diffusion-limited current falls in the voltage range from -0.7v to -1.0v vs. silver-silver chloride electrode (see figure 6).

5.6 The Laboratory Model Cell

5.6.1 Parts

The laboratory model cell which is being delivered to the Jet Propulsion Laboratory as part of the contract is seen in figure 3. It consists of the following components:

- a. The membrane -- E. I. Dupont deNemours, 0.5-mil sealable Teflon film.
- b. The cathode (polarizing electrode):
 - (1) Beckman No. 39273, platinum inlay electrode.
 - (2) Fisher No. 11-505-85, sealed platinum electrode.
- c. The anode (reversible, non-polarizing electrode) -- silver-silver chloride wire made prior to use with available silver wire.
- d. Electrolyte -- 70 cc H_2O and 5 grams KCl, made up to 100 cc with methanol.
- e. The cell proper -- utilizes a custom-made glass tube connected to a special glass-O-ring seal (Kontes Glass Company, Vineland, New Jersey), No. 67175, size 28/15 joint (Viton O-ring).
- f. Clamp -- size 28, Konte's Glass, No. 67500, to seal together: glass-O-ring-glass.

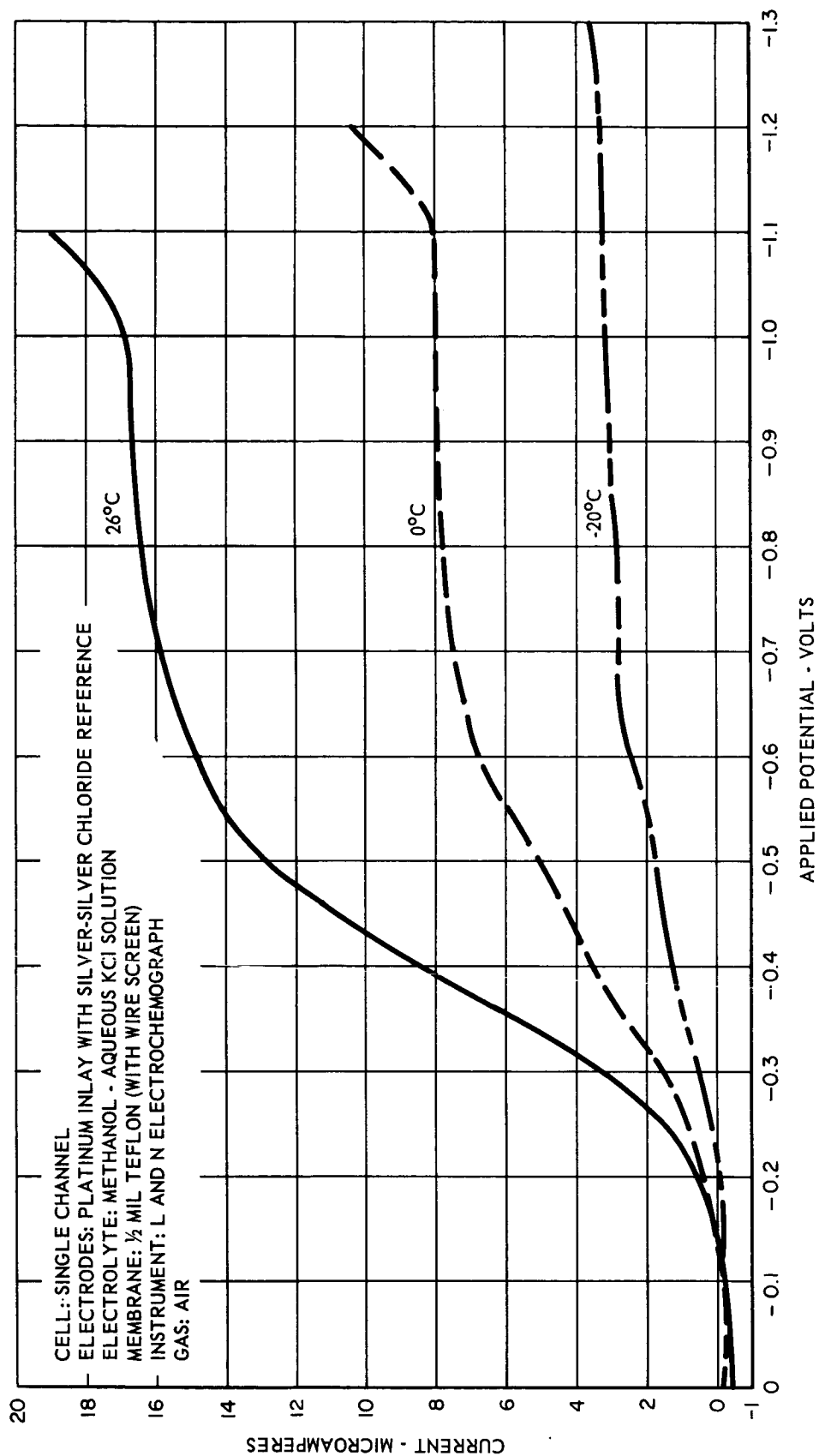


Figure 6. Temperature Polarographs

5.6.2 To Assemble Cell

- a. Immerse platinum inlay electrode in a fresh warm 1:1 HNO_3 solution.
- b. Clamp bottom part of glass-O-ring with o-ring channel facing up.
- c. Place Viton O-ring in proper channel.
- d. Place electroformed screen on O-ring.
- e. Cut piece of 0.5-mil Teflon and place on O-ring.
- f. Place another Viton O-ring on membrane.
- g. Place glass cell with O-ring channel down so as to fit this channel over O-ring.
- h. Clamp together top and bottom with clamp and screw down tight -- the cell housing is now assembled.
- i. Make up silver-silver chloride electrode in the following manner: Make a spiral of silver wire by wrapping it around glass tube. Wash the silver wire in acetone, rinse in distilled H_2O , place in a beaker of 0.1-N solution of HCl , KCl or NaCl , add a platinum screen or sheet to serve as cathode, connect a battery across the two electrodes with + side connected to the silver wire for oxidation and -side to the platinum sheet. Adjust the voltage so that the current density is approximately 100 ma/cm^2 and pass current until dark coating is uniform and substantial. Remove and rinse in distilled H_2O . Silver-silver chloride electrode is now ready for use.
- j. Rinse platinum electrode in distilled water.
- k. Insert a rubber stopper large enough to fit into the glass chamber.

l. Insert silver wire in the rubber stopper in such a manner that the platinum inlay electrode is situated within the spiral.

m. Pour the electrolyte (70 cc H_2O , 5 grams, KCl, make up to 100 cc with methanol) into the glass cell.

n. Bubble purified grade nitrogen through the electrolyte for 5 minutes.

o. Place the electrode, pack loosely over the cell top, and continue bubbling nitrogen for another 5 minutes.

p. Place the stopper in the top of the cell firmly so that the platinum inlay electrode is sealed firmly against the membrane and screen.

q. The cell is ready.

A word of caution: When the electrode is removed or when there is excessive movement of the platinum against the membrane, the membrane should be replaced.

The technique used in determining whether the cell is performing properly is the following. Determine the diffusion current on room air under ambient conditions by applying 0 - 1.2v stepwise and by measuring the current at the various voltage levels. Choose a potential that is somewhere near the middle of the diffusion current plateau. This is the polarization voltage which will then be used. Pass prepurified nitrogen through the chamber to establish that the cell is sensitive to oxygen. The current should approach zero at the polarization voltage chosen. Then pass air into the chamber and note if it returns rapidly to the same current as before. If this occurs the cell is working properly.

In the case of the supplied laboratory model, the polarization voltage was -0.75 vs. silver-silver chloride electrode and the current for ambient air was 10 - 15 μa .

5.7 Test Procedures

5.7.1 Flow Systems

Figure 7 is a photograph and figure 8 a schematic drawing of the first general flow system employed. It provided a means of mixing gases to send to the oxygen detector to measure O_2 sensitivity and contaminant determinations. When Tank B was 1% O_2 -99% N_2 the gas could be diluted in ratios of 1:100 in two steps to determine a sensitivity of 0.0001% oxygen. During the contaminant runs N_2 , Ar and CO_2 were used. The flowmeters are of the orifice type and are used for low flow rates of gases. There was provision for larger flow rates also. The flow rate to the detector was generally 200cc/min.

Figure 9 is a photograph and figure 10 a schematic drawing of an environmental flow system designed to simulate the descent tests. This system also allowed the mixing of gases to obtain various sensitivities of oxygen as well as mixing for contaminant determinations. In addition, it had a means of pumping out the cell chamber. Thus the same contaminant and oxygen mixture could be determined at the lower pressures (1-100mm Hg).

The procedure for operation was to first set the flow rates for the desired mixing of the oxygen-containing or contaminant-containing mixtures. Then the whole system was evacuated all the way back to the stop-cock before the orifice flowmeters, to eliminate all undesirable gases from the entire system. If necessary, gases were flowed through and this step was repeated. Then the mixture of gases was flowed through

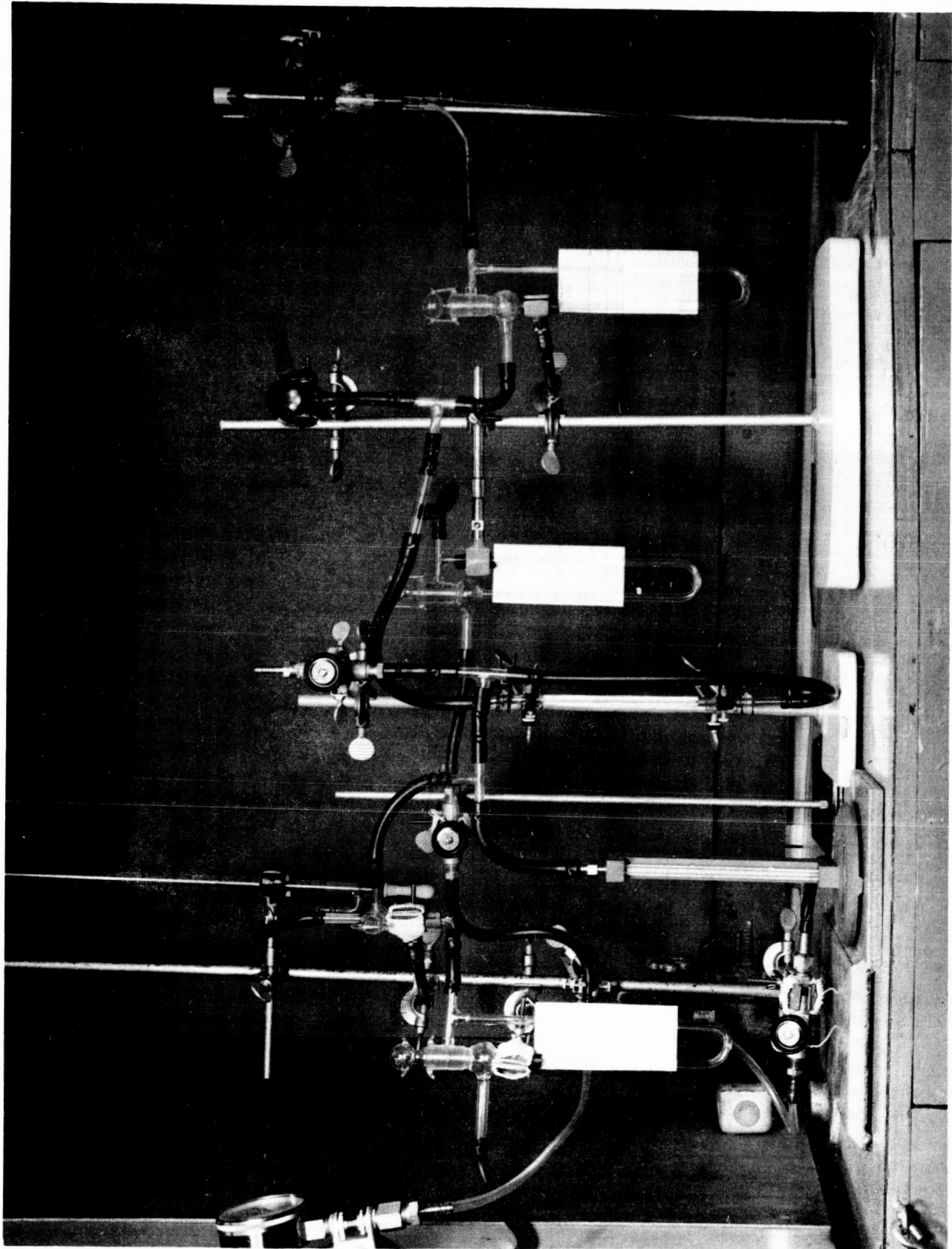


Figure 7. Atmospheric Flow System

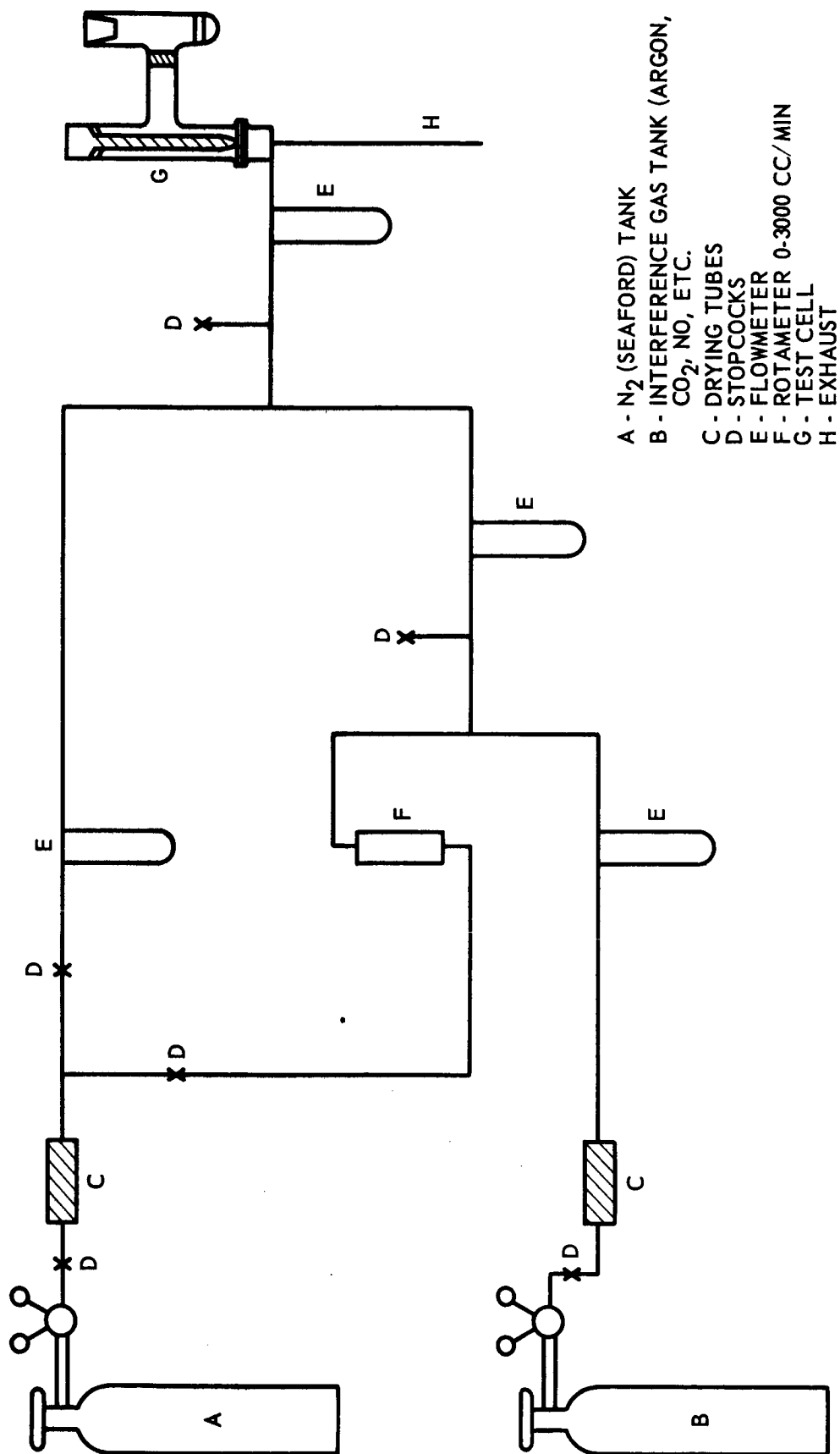


Figure 8. Atmospheric Flow System Schematic

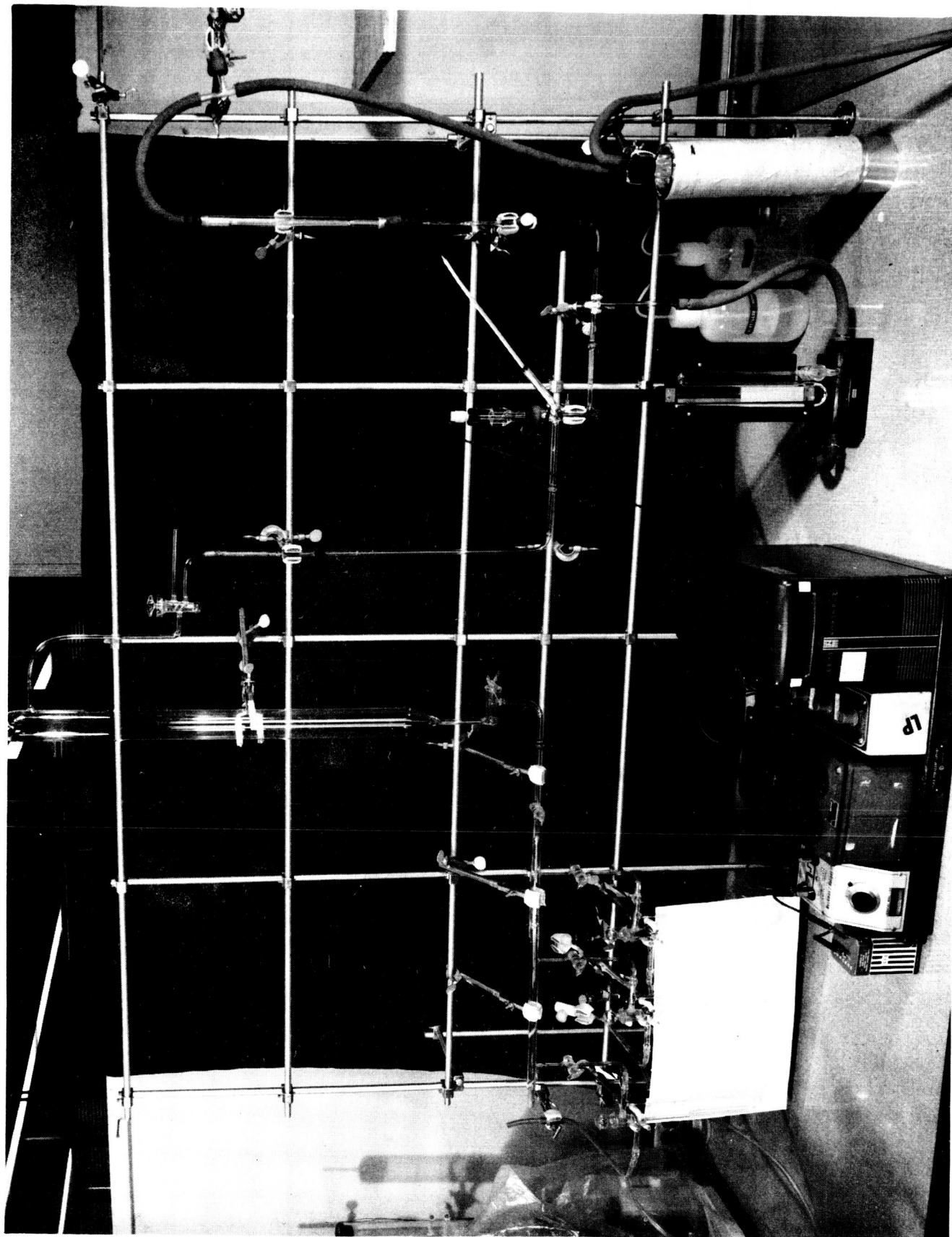


Figure 9. Vacuum-Flow System

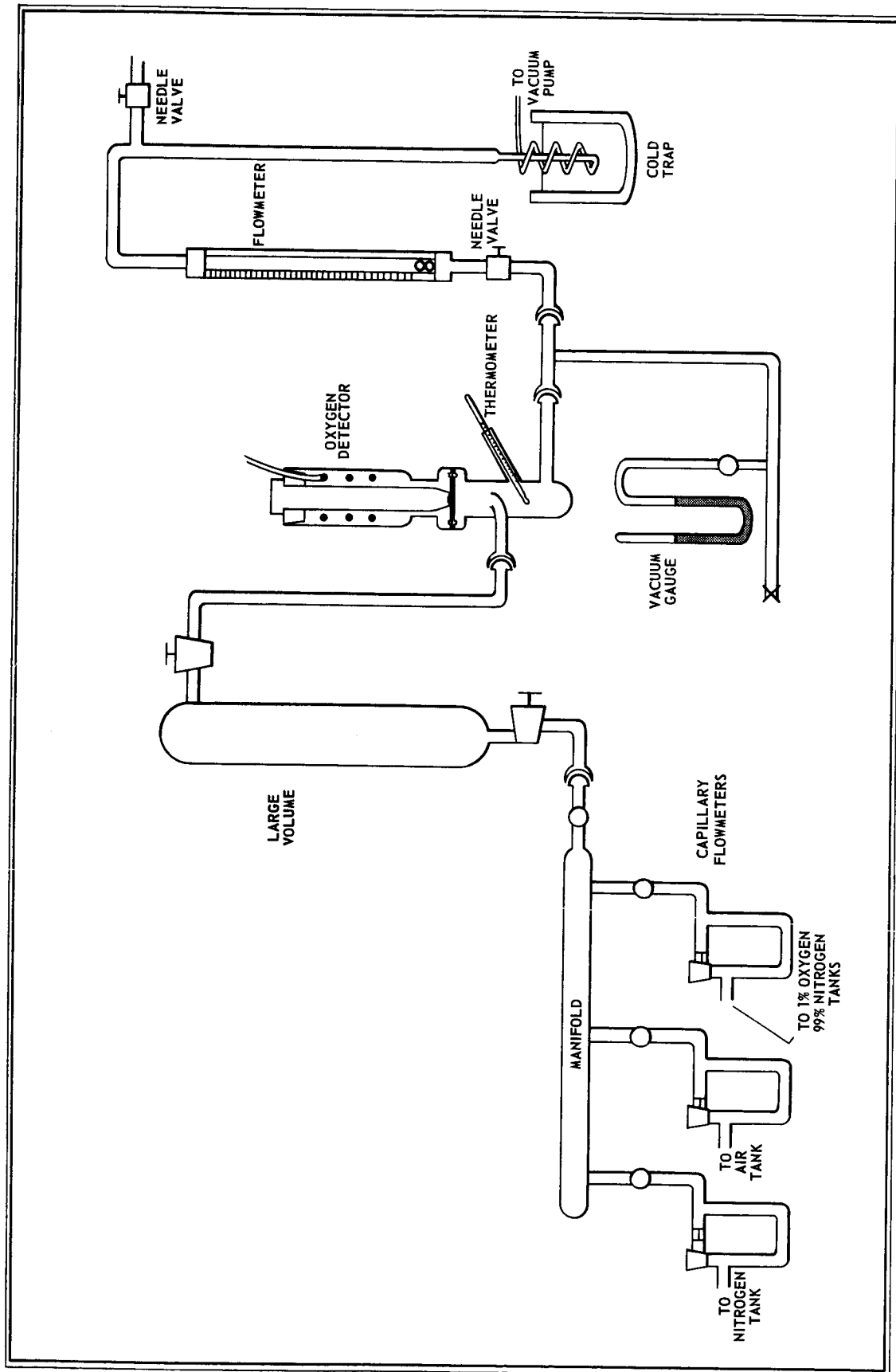


Figure 10. Vacuum-Flow System Schematic

the mixing chamber, through the large volume and through the detector chamber, where the measurement of O_2 concentration could be made at one atmosphere. When this factor was determined and found to be steady, the stopcocks at both ends of the large volume were closed and the cell chamber and parts were subjected to the vacuum. When a high enough vacuum was achieved, and with the vacuum pump still connected to the cell chamber, but barely working on the chamber due to the partially closed needle valve before the flowmeter, the stopcock on the large volume container nearest the cell was opened slightly to increase the pressure in the detector chamber. In this case, the pump was drawing slightly on the gases in the large chamber and flowing them through the detector chamber. The total pressure was read on the vacuum gauge directly in line with the detector chamber. Note that the inner part of the cell was not subjected to the low pressure, and further that the electrolyte did not leak out. Also, the membrane was not affected. The cell was capable of working at lower than 1mm of Hg pressure.

The current, after exhausting and rinsing with nitrogen gas and then evacuating to below one atmosphere, was 0.004 ua on the laboratory model cell. This is possibly a background current, or might be an actual oxygen determination since the lab model cell was not a completely sealed system. O_2 creeping from the air is capable of giving a reading even though nitrogen appeared to be the only gas in contact with the cell chamber.

The cold temperature runs could not be made with this system, since the vacuum pump removed practically all the gas and there was too little gas left to conduct. This low temperature work was done separately by wrapping a copper tube to a coil and placing it in a Dewar with dry ice and acetone. The temperature of this mixture was -70°C and served to cool the air in the tube. The fresh air was flowed through this tube directly into the cell chamber and out into the room. The temperatures in the detector were found to be as low as -25°C . Lower temperatures could be achieved, if desired, by changing the flow rate of the gas.

5.7.2 Electrical Instrumentation

There were two polarographic instruments available whose capabilities were utilized to the fullest extent. The Fisher Elecdropode and the Leeds and Northrup Electrochemograph were both mentioned earlier (see figures 4 and 5). The Elecdropode had a current measuring capability of $2.2\text{ }\mu\text{a}/100$ divisions to $1.1\text{ }\mu\text{a}/100$ divisions and the Electrochemograph from 1 - $100\text{ }\mu\text{a}$ full scale. The lowest current that could be determined was $0.01\text{ }\mu\text{a}$ in either case. Utilizing the platinum inlay electrode with the $3/8$ inch diameter surface, lower currents were required to be measured.

The circuit in figure 11 was utilized for this purpose with the similar component structure of the Elecdropode, but with the most important change being a Leeds and Northrup Galvanometer (No. 2431-H) with the capability of determining currents to as low as $0.0004\text{ }\mu\text{a}$. This circuit is simply a power supply with a divider to vary the voltage,

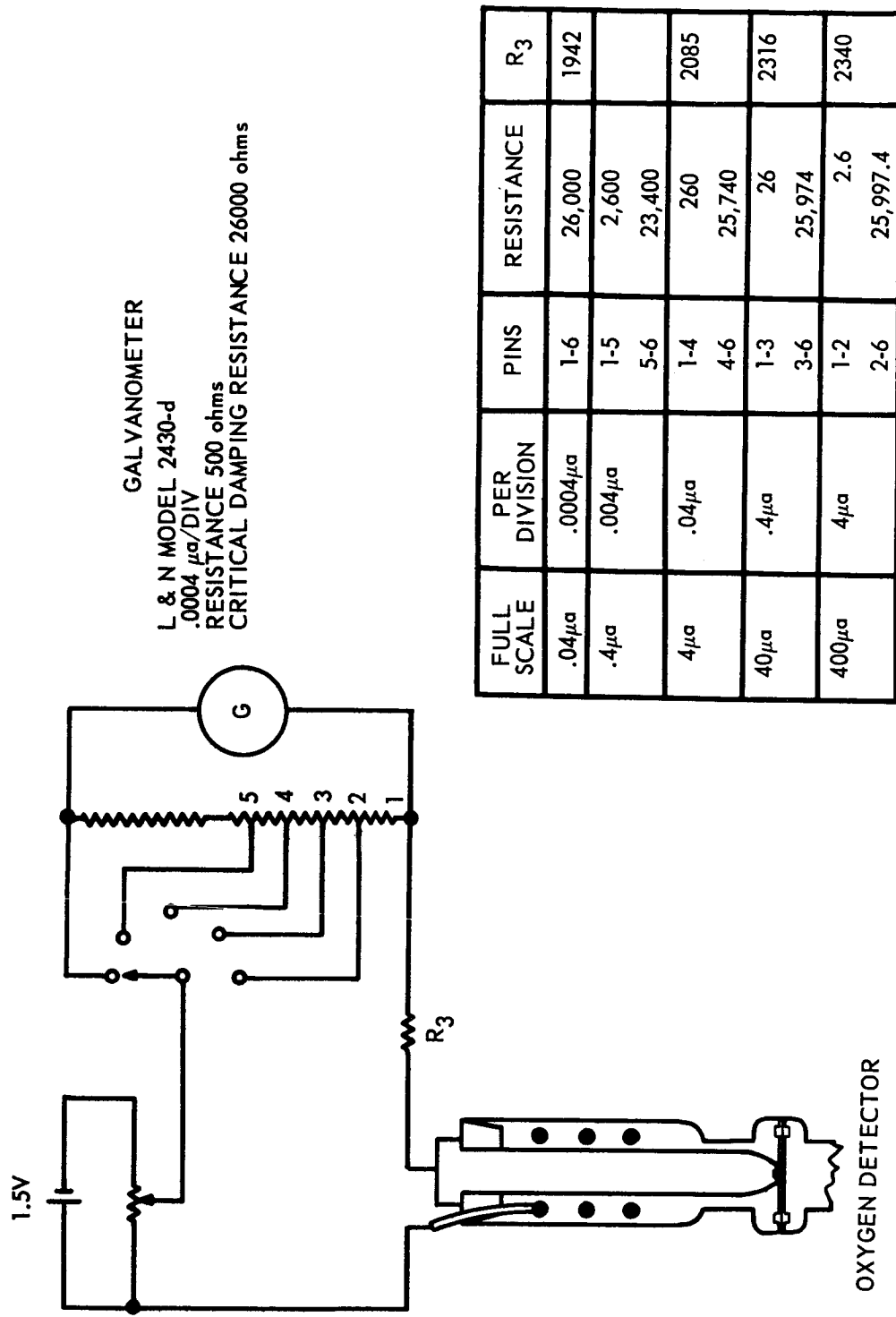


Figure 11. Bridge Circuit for Current Measurements

and a current measuring circuit. By changing the position of the switch, sensitivities could be changed in decade steps from 0.0004 $\mu\text{a}/\text{div.}$ to 0.004 $\mu\text{a}/\text{div.}$ etc. to as low a sensitivity as 4 $\mu\text{a}/\text{div.}$ The additional resistor R_3 was included to maintain the same resistance in the circuit over all the ranges.

A note of caution, is that the current should not be read in the circuit with voltage leads connected across the cell even with the very high impedance Keithley Electrometer because at the lower currents the impedance of the cell approaches infinity. This causes the Keithley Electrometer to drain some current and thus give a false indication of the current passing through the cell.

5.8 Parameters and Results

5.8.1 Temperature

The specified temperature requirements included a sterilization temperature of 145°C for 24 hours and for the cell to operate in the range of -20°C to +20°C.

The parts of the cell individually will withstand the sterilization temperature for the 24 hours. The electrolyte will not be in the cell during this time and it is presumed that it will be contained in a separate chamber capable of withstanding 300 psi. The membrane, as mentioned earlier, withstood the test and worked well in the cell afterwards. The electrodes are also stable over the temperature range.

To meet the cold temperature requirement, the electrolyte mentioned above was utilized and operated satisfactorily under the operating temperature conditions specified. In figure 6 are found

polarograms at +20°C, 0, and -20°C which were obtained using the H₂O-methanol-KCl solution. As expected from the literature, these diffusion currents are not linear and a temperature calibration will have to be made for the individual cell.

5.8.2 Pressure

The cell is expected to operate under reduced pressures of 10 to 100 mm of Mercury. The cell has been found to operate well within these limits and at even lower pressures than 1mm of Hg. It will also work under ambient conditions of 760mm. The electroformed screen holds the Teflon membrane in place while under the influence of the reduced pressure. Even though the inner parts of the cell are at 1 atmosphere, the diffusion of the oxygen from the lower pressure to the higher is evident in the sensitivity determinations at the lower pressures. There is no electrolyte leakage through the membrane in spite of this gradient.

A graph of air pressure vs. diffusion current over the range 10-100 mm of Hg is seen in figure 12. As can be noted, a straight line relationship holds until the very low pressures where the presence of small quantities of atmospheric oxygen appear to have found their way into the cell. This straight line relationship has been shown for the lower oxygen concentrations but nonlinearity does occur at the higher oxygen pressures.

The current for ambient air can be multiplied by the fractional amount of pressure (for example $10 \text{ mm} - \frac{10}{760}$ $100 \text{ mm} - \frac{100}{760}$) to estimate the current at the lower pressures.

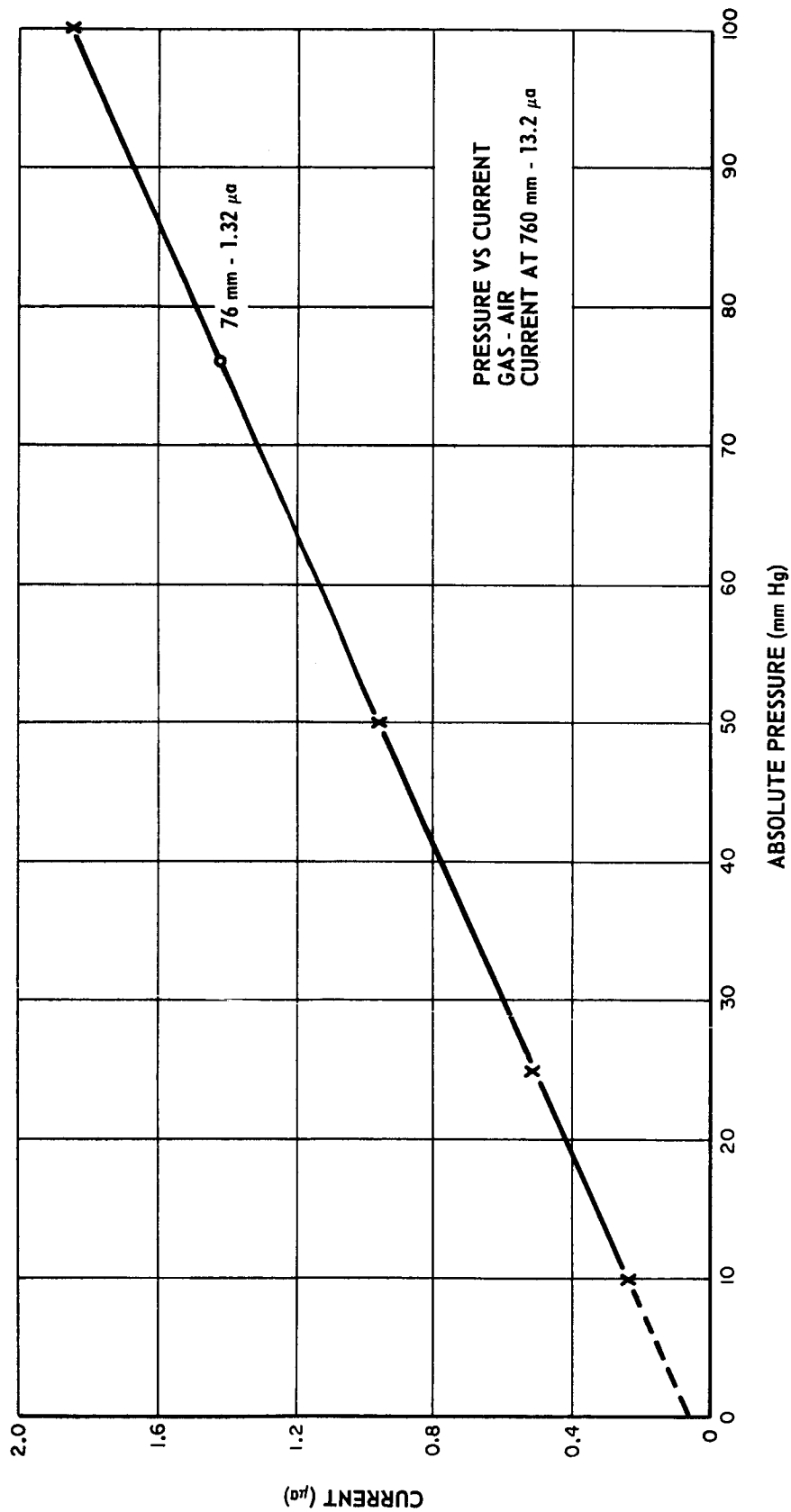


Figure 12. Oxygen Pressure Sensitivity

5.8.3 Sensitivity

The predicted range of oxygen concentrations for the Martian atmosphere is expected to be well within the 3 decade range of 0.001% to 1% oxygen chosen for study purposes on the polarographic detector.

The sensitivity experiments always began with a determination of air (21% O_2) since it was readily available. However, the most interesting experiments were conducted over the ranges:

0.001% to 0.01% O_2

.01% to .1% O_2

.1% to 1% O_2

The results were found to be linear, as noted in figure 13, at 1 atmosphere of pressure. As one reaches the lower oxygen concentrations, the atmospheric oxygen must be considered because of small leaks through seals, etc., which tend to give a higher current reading. The laboratory cell was sensitive to these three ranges of concentrations, and it was noted that a linear relationship exists so that one may multiply the ambient air current by the fraction of the 21% oxygen used to determine a predicted current (for example for 1% O_2 , multiply the current in μa by 1/21).

5.8.4 Response

No specific requirements were listed for this parameter. However, response is relatively fast for a polarographic cell with a platinum electrode as the sensitive cathode. An estimated time of response is one second. The response as noted early in the testing was not a good indication since a time period was required for a new concentration

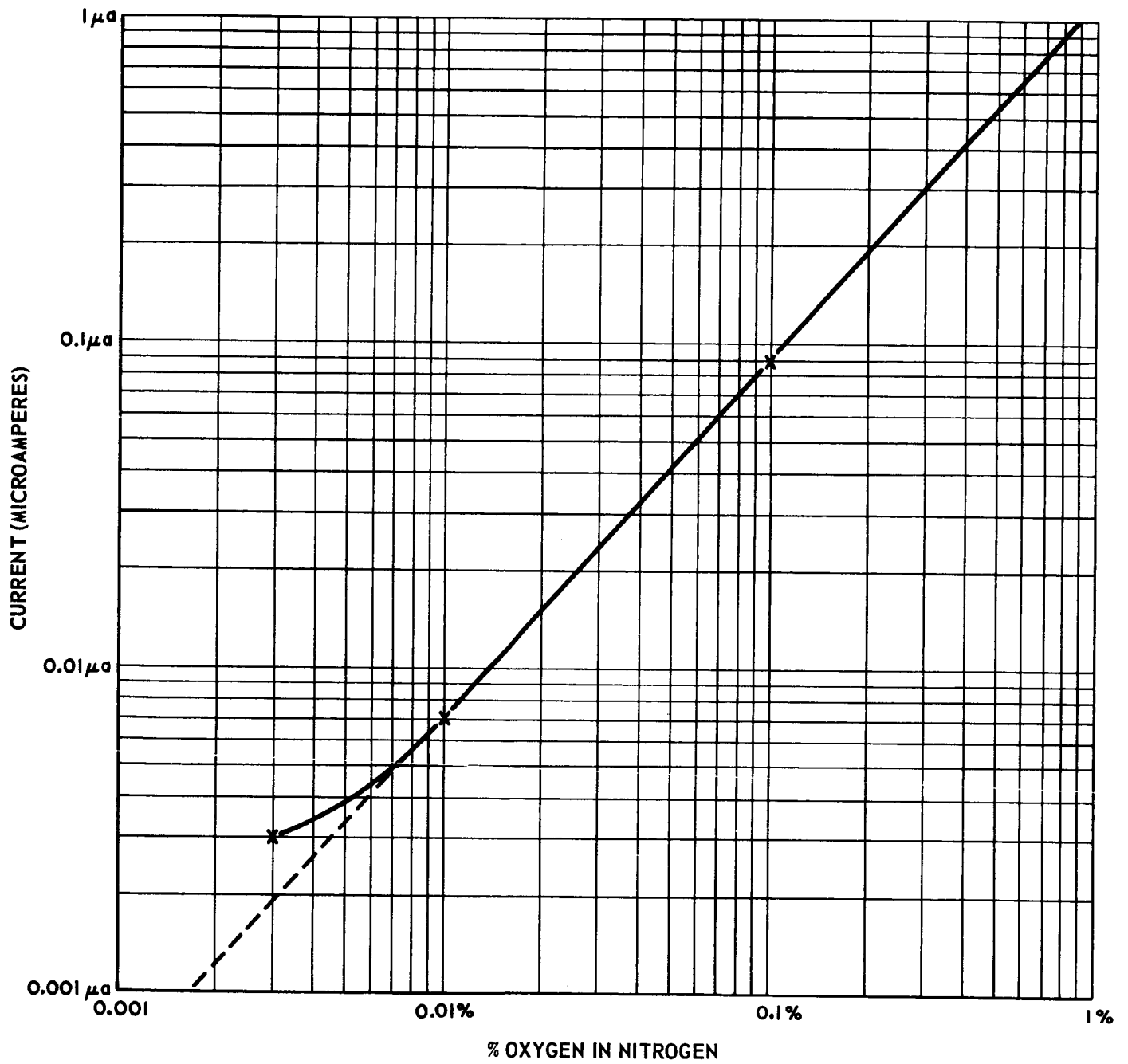


Figure 13. Oxygen Concentration Sensitivity

of gas to enter into the detector chamber. The flow systems were long and the replacement of gas was slow. However, from the low pressure tests in which the gas mixture fills the evacuated system almost instantly, the current change is so fast that one observer is required to watch the current, while another manipulates the stopcock.

5.8.5 Interferences

This test was to determine sensitivity to interferences of Nitrogen, Argon, Carbon Dioxide and Ozone.

Nitrogen and argon function as inert gases that are not reduced at the cathode in the detector, and thus were utilized as suitable dilution gases for sensitivity determinations. Carbon dioxide was reduced at the polarizing electrode but at greater concentrations than 1% carbon dioxide in nitrogen. This is far in excess of the expected value of 0.1% carbon dioxide. Sensitivity to ozone was a specific requirement. A special flow system had to be designed to generate ozone, and determine its concentration.

The most satisfactory method⁶⁷ found to test the effect of particular ozone concentrations upon the oxygen electrode response entailed the use of the apparatus as pictured in figure 14, and schematically in figure 15. The system is described as follows:

A 1% oxygen mixture (1% oxygen-99% nitrogen gas) is passed into an ozone generator. This ozonator (o) consists of a Hanovia mercury-vapor tube enclosed in a glass condenser, and powered by a 3000 volt luminous transformer. The gas flow rate is determined by the ozone flow meter (F_1) which contains dibutyl phthalate. The

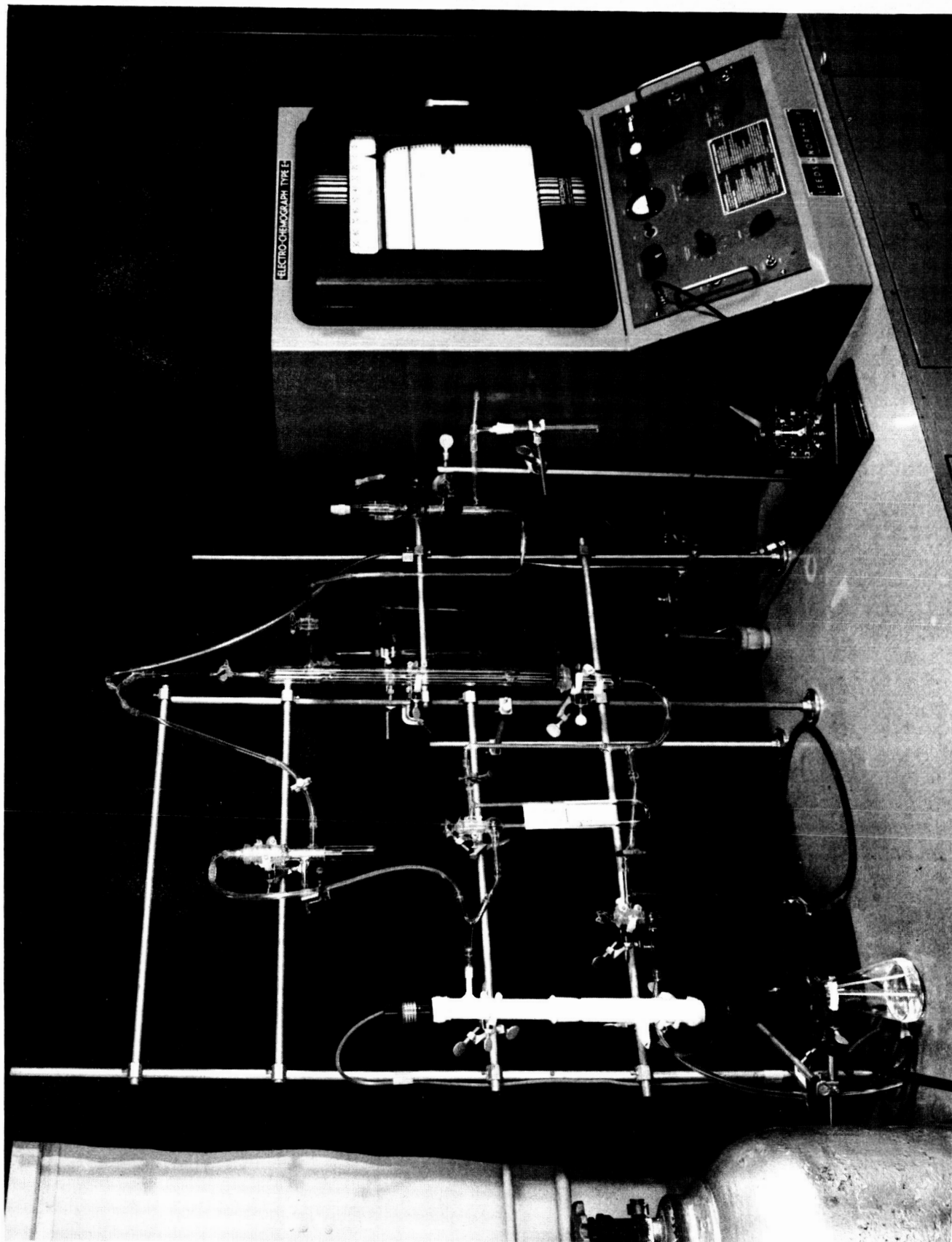


Figure 14. Ozone Flow System

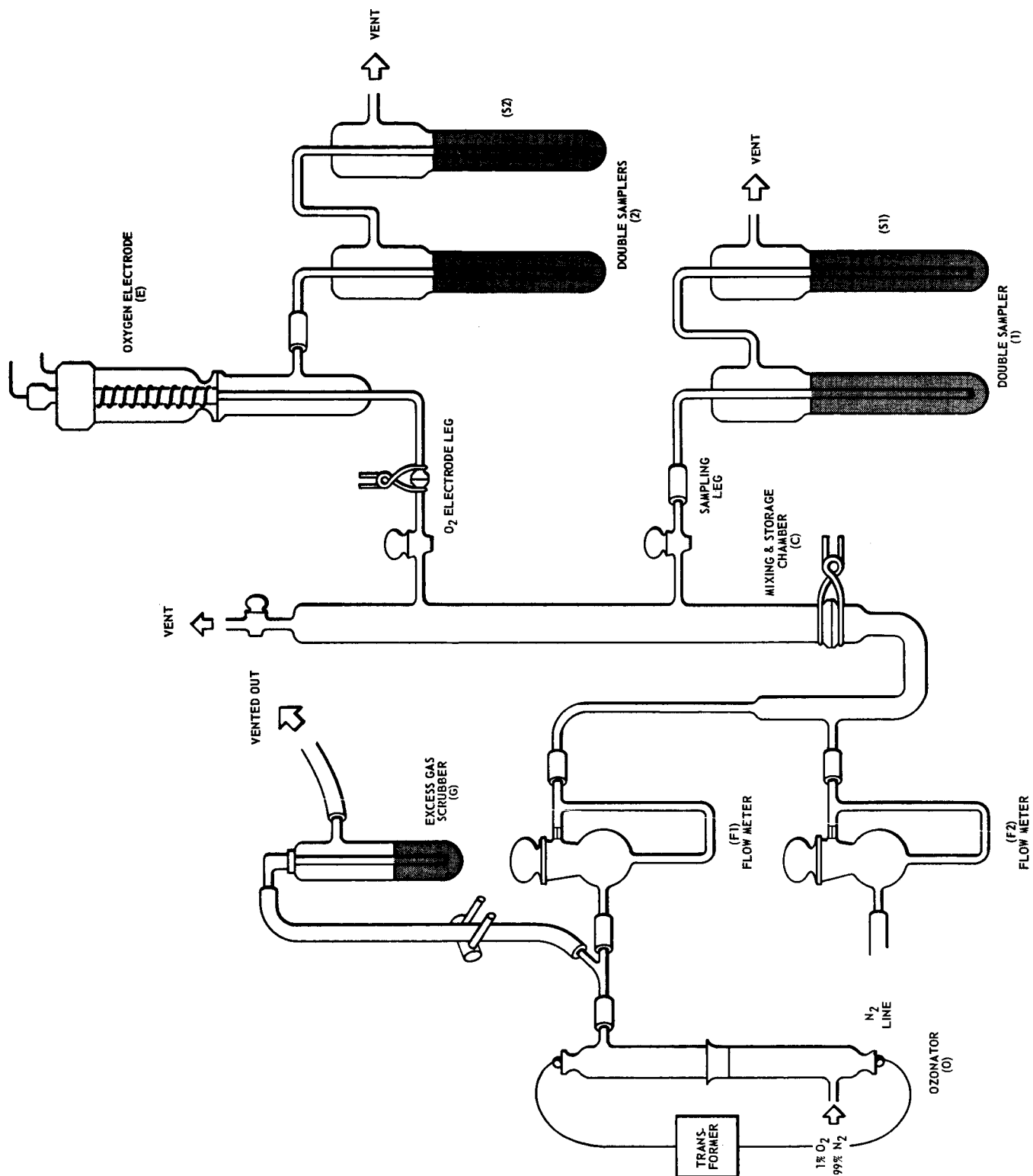


Figure 15. Ozone Flow System Schematic

ozone then passes into a mixing and storage chamber (c) from whence it can be delivered either to the oxygen electrode directly through one leg or through a sampling leg to a concentration sampling apparatus (s_1).

Initial polarographic runs were conducted over the range of -0.6 to -1.0v vs. saturated calomel electrode and recorded on a Leeds and Northrop Electrochemograph to establish the diffusion current of the oxygen electrode. After this had been determined, the ozone generator was started. Within 20 seconds ozone was passing through the oxygen electrode and outlet gases were bubbling through the after-sampling tubes (S_2). Control of ozone production was regulated by the flow rate of the 1% oxygen gas mixture through the ozonator. Increasing ozone concentrations were imposed upon the oxygen electrode system until one particular ozone concentration registered some effect. Once this level of ozone was reached, a detailed analysis of the ozone concentration, before and after contact with the oxygen electrode, was initiated by use of the sampling tubes (S_1 and S_2). The sampling apparatus consisted of two pairs of gas bubblers each containing 8.0 ml of a 1% KI in neutral phosphate buffer medium.

The ozone concentration was determined spectrophotometrically by measuring the amount of iodine liberated by the ozone. Standard graphs of absorbance vs. iodine (or ozone) were plotted from optical density readings from a series of prepared standards. The ozone equivalent was calculated on the basis of $O_3 \cong I_2$ (1 ml of 0.01N $I_2 \cong 240 \gamma$ of Ozone).

The ozone was bubbled through these gas samplers for 10 minutes at a predetermined rate. Then the contents were transferred to a 25 ml volumetric flask, acidified with 2 drops of concentrated H_2SO_4 and brought up to volume with a neutral phosphate buffer solution. The sampling solution was allowed to stand for 15 minutes before determining its optical density in a Beckman DU spectrophotometer at 352 m μ .

These results give the ozone concentration after passing the Teflon membrane. The ozone concentration which entered into the oxygen electrode was determined by switching the flow of ozone from the oxygen electrode directly to the sampling tube by stopcock manipulations on the storage chamber (c). Once again the ozone was bubbled for 10 minutes through the other pair of gas bubblers.

The complete characterization of the ozone concentration, before it entered and after it passed the oxygen electrode, indicated a lower ozone concentration after passage through the electrode chamber.

This would strongly suggest one of two possibilities--(a) the possible dissociation of ozone when it comes in contact with the Teflon membrane on the inner surface of the oxygen electrode; thereby releasing oxygen, and (b) the possible leakage of ozone around the membrane, thereby giving an erroneous lower ozone concentration in the after-samplers.

The experimental results shown in figure 16 indicate that at a flow rate of 864 ml of the 1% oxygen mixture per minute, the diffusion current was equal to 0.93 μ amps. This is equivalent to 11.47 mg

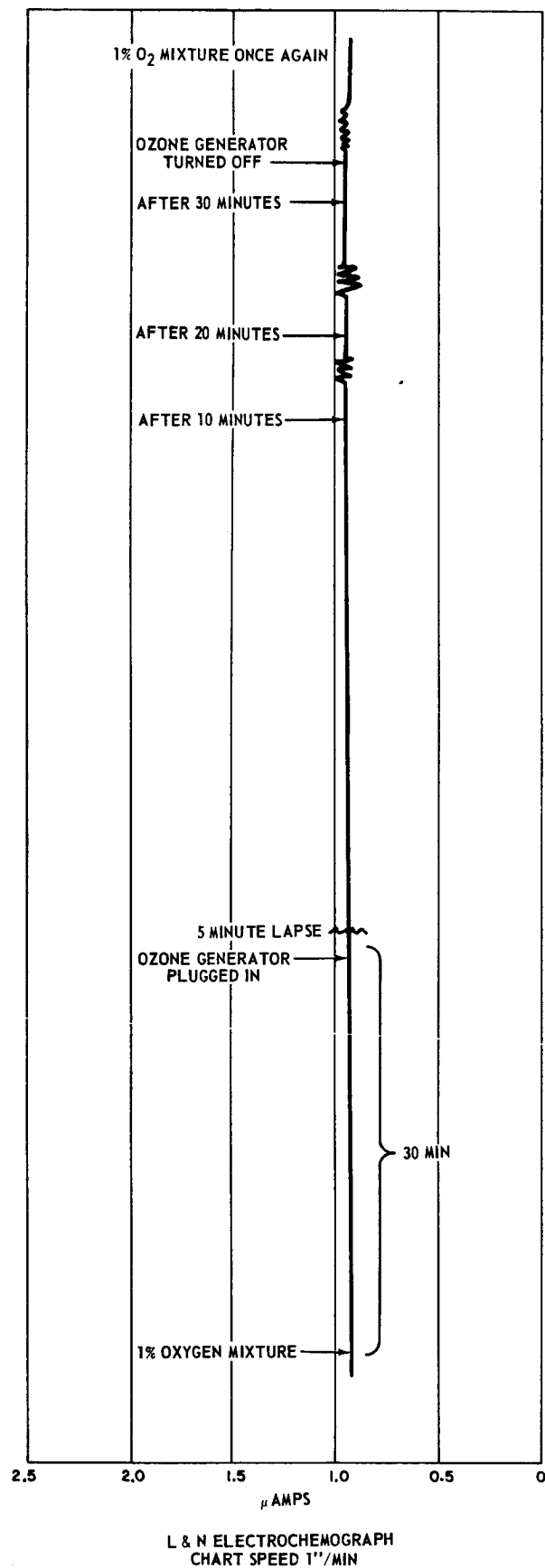


Figure 16. Ozone Sensitivity Results

of O_2 passing into the electrode chamber per minute. This 1^o/o mixture was flowed for 30 minutes. Then the ozone generator was turned on for 30 minutes. The ozone concentration which had an effect on the electrode's current was experimentally determined as 1.22 mg ozone per minute. This indicates that approximately 10^o/o of the oxygen was converted into ozone or 0.1^o/o of the total gas mixture. The current, after flowing the 0.1% ozone concentration through the electrode chamber for 10 minutes, rose to 0.96 microamperes and maintained this value for two successive 10 minute readings, as shown in figure 16.

After the 30 minutes of ozonizing, the generator was cut off and 1% oxygen mixture remained flowing. The current was then seen to return 0.94 microamperes very close to its initial value of 0.93 microamperes.

It is concluded, from these results, that the polarographic oxygen electrode is affected by higher (0.1%) concentrations of ozone, and then only a slight change is noted.

6. BREADBOARD DESIGN

Going beyond the scope of the contract, it was decided to build a first-cut breadboard model incorporating the electrochemical cell, electronics, and associated parts that would conform to the required specifications for size, power, and, with some reservations, weight. The size of the package was determined by the specified volume of 500 cc and was chosen as 4" x 4" x 2". This was divided into two sections, 4" x 2" x 2" each; the cell and associated parts in one section, and the electronics in the other. This unit was to be a working model. However, time did not permit the completion of the associated parts to the cell. To be supplied along with the laboratory model of the cell, will be the crude breadboard version of the cell, an amplifier, and mock-up version of the associated cell parts. These three major components are discussed below.

6.1 Cell

The cell design was to be altered from the laboratory model in two respects. First, it had to be scaled down in size to fit into the allotted 4" x 2" x 2" compartment with the other parts. Second, the platinum electrode surface area had to be increased to develop a larger diffusion current than the laboratory model. The current in the laboratory model was too low to detect very low oxygen concentrations at extremely low pressures. The decision was to increase the electrode area to that of a circle 1 inch in diameter. Another change was to place beneath the platinum sheet a fine platinum screen, so that the effective area of platinum electrode would be even greater. The silver-silver chloride spiral was utilized as well as the 0.5 mil-Teflon membrane and the prescribed electrolyte.

The changes resulted in the increase of the diffusion current from 10 - 15 μ a on ambient air to 532 μ a. Strangely, the cell current dropped very soon after this reading and the cell became insensitive to oxygen. Upon disassembly of the parts, it was determined that the surface area of the silver-silver chloride, which had been reduced for size limitations, was too small, and polarization was taking place on this electrode as well as on the platinum. (See section 5.4 on anode requirements.) An alteration was made in the cell assembly and a larger silver-silver chloride electrode utilized. The current on ambient air was again 532 μ a and steady. Nitrogen was passed through and the current dropped immediately to a low value of 10 μ a. It is felt that this "background" is high, but this indicates its sensitivity to oxygen. Further experimentation remains to determine whether this is a true background current or is caused by interfering oxygen from leakage or a combination of both.

6.2 Breadboard and Design Amplifier

The oxygen detector cell in a high O_2 environment, such as that of the earth's atmosphere at sea level, has an adequate output requiring little adaptation to meet the needs of a reliable telemeterable signal. As the concentration of O_2 decreases to orders of parts per million, the output decreases proportionally, and larger amplification factors are found necessary to meet the telemeterable form. This low level output, of course, is not limited to the O_2 cell, but is found in photomultiplier tubes, vacuum gages, ionization gages, and ion chambers, to mention just a few. The devices generally have their outputs restricted down to 10^{-6} to 10^{-13} amperes. A survey of voltage and current amplifiers reveals

two basic methods of amplification; either a chopper-ac amplifier-rectifier or a dc electrometer. As a possibility without prejudice, a chopper-ac amplifier was experimentally attempted. In an attempt to eliminate additional components and simultaneously conserve power, the voltage to the cell was square wave voltage switched at 1 kc and the O_2 concentration from 0.02% to 20%, and no change in output from the cell was detected. Placing the chopper after the cell was considered. This would involve adding a gate to interrupt the dc signal output. The chopper-ac amplifier was relinquished at this point upon the following considerations:

a. There was an inability of this additional gating component to switch currents of this magnitude, reliably, without going to a vibrating reed capacitor--the gate would potentially be the most vulnerable point in the circuit in case of component failure.

b. The unfavorable temperature dependence of the chopping rate which would slightly increase temperature correction factors.

c. This is a dynamic system that requires an oscillator to start.

In preliminary analysis, the dc electrometer was found the most satisfactory amplifier to be investigated from considerations of power consumption, size, and complexity.

The vacuum tube electrometer tube was chosen in the initial laboratory design. This component was number CK 5886 by Raytheon as recommended on JPL spec. no. 20061A. The electronic configuration was of a dc differential amplifier with three stages of parallel amplifiers, including the vacuum tube first stage. The vacuum tube input was required, since present day silicon transistors do not have the necessary current stability and noise figures.

Stability was recognized early to be an important consideration in the design and development. A slightly modified version of the stable Beneteau circuit was experimentally built, retaining, of course, the stability characteristics. Adaptation was required to match the vacuum tubes to the first stage transistors. The first version operated the tubes as triodes. (Refer to figure 17.) The second version (figure 18) incorporated the second grid, making a better match to the transistors and improving the signal-to-noise figure. This was achieved by operating the input tubes as pentodes, which improved the match between the first and second stage, consequently improving the noise figure. At this time in the amplifier development, improvements in the basic cell design led to greater quantities of current available to measure the same O_2 concentration. The relaxation of the prior current requirements allowed the input to be fed directly into the transistors. The range of current measurements were design-frozen at 1.000% oxygen, giving 1.000×10^{-6} amperes output from the cell with a linear line relationship to 0.001% oxygen yielding 0.001×10^{-6} amperes output from the cell. (Room temperature, standard pressure.) From the Appendix (part 1), the range of current under the worst case consideration is 3.34×10^{-6} amperes to 1.11×10^{-10} amperes. Corresponding cell impedance is 212 K ohms to 6,360 megohms. Minimum perturbing loading resistance was experimentally found to be 5,000 ohms using a laboratory cell operating on the atmosphere at 0.5 volts applied potential with internal impedance of 25 K ohms. This ratio should follow in a valid relationship to the prototype configuration yielding 41.4 K ohms for the minimum perturbing cell impedance calculation. All

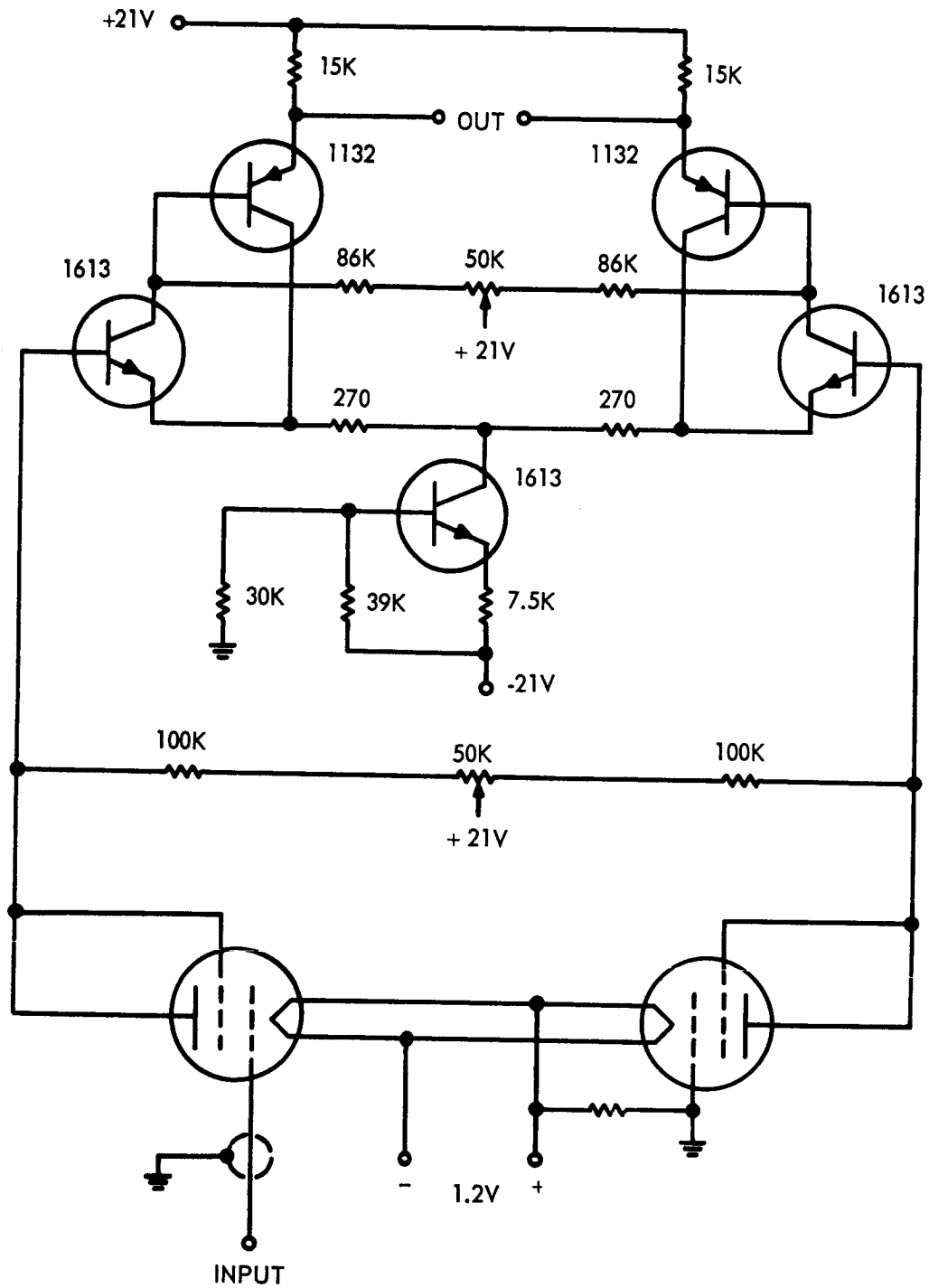


Figure 17. Circuit Diagram Triode Fire Stage

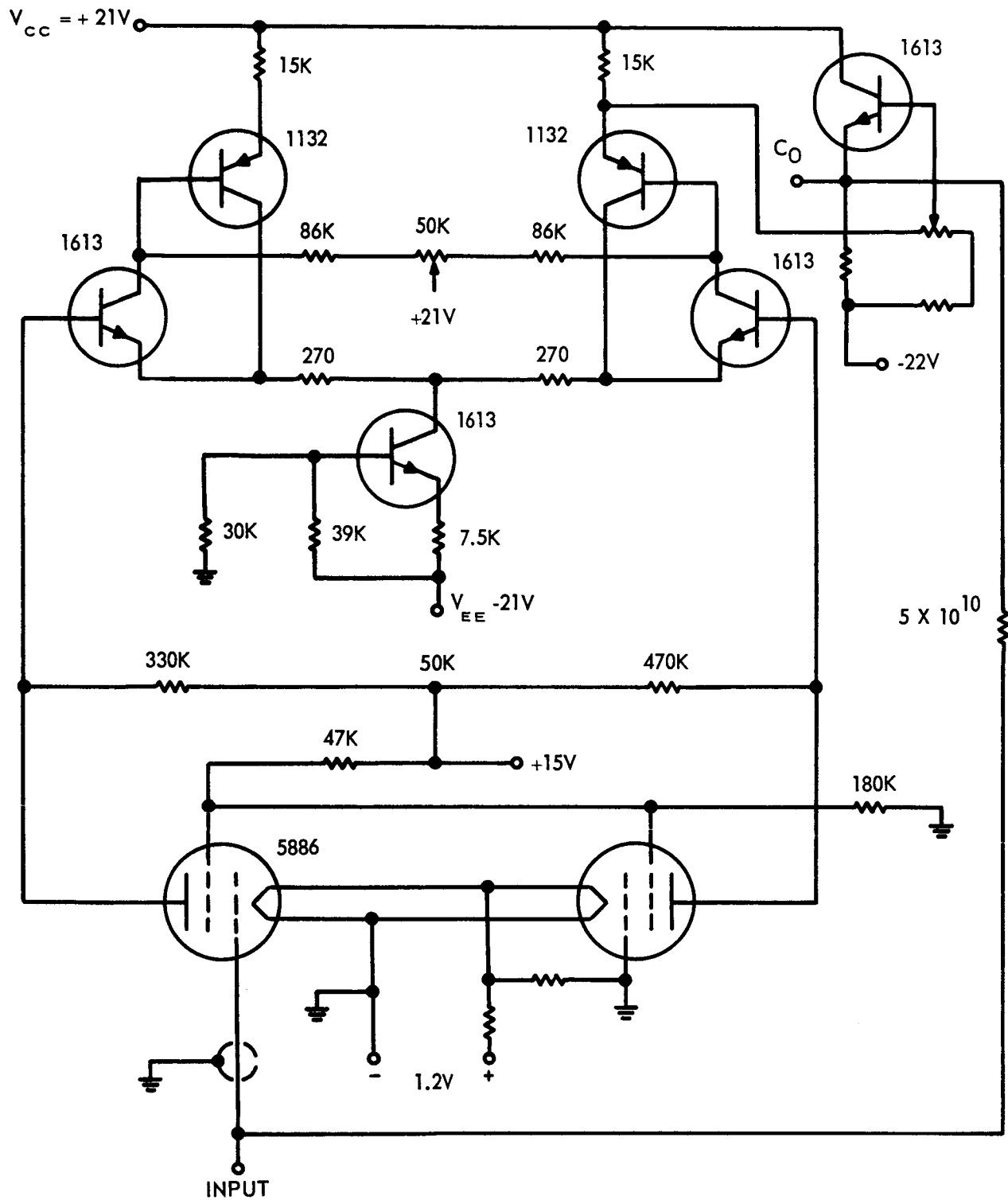


Figure 18. Circuit Diagram Pentode First Stage

actual cell loading must be below this value. Considering this a design value, 30 K ohms was picked as a value not to be exceeded for the amplifier input impedance. The output impedance has been established by the telemetry system to be 5 K ohms. The amplifier supply voltage designed value was 21 volts to allow for low voltage variation from 28 volts. Upon the foregoing considerations, an experimental prototype was constructed using all JPL spec. no. 20061A approved components. The circuit (figure 19) was integrated with the prototype cell and performed satisfactorily. The local cell supply, in the initial integration, was a battery and a 20 K ohm voltage divider. This would be most conveniently replaced through a zener diode regulator circuit recommended in section 7.2. The circuit analysis is carried out in Appendix, part 2.

It can be shown that the stability is superior in comparison to the conventional Slaughter circuit. The Slaughter circuit based upon the same circuit assumptions plus

$$R_{EE} \gg R_E + R_S \quad \text{and} \quad \frac{R_{E2}}{2R_{EE}} \ll 1$$

can be shown, with considerable effort, for the first pair to be

$$e_o \approx \frac{2(R_{L1} + R_{L2}) h_{FE1} h_{FE1}'}{R_S (h_{FE} + h_{FE1}') + R_E (h_{FE1} h_{FE1}')} \left[(e_1 - e_2) + \left\{ \Delta V_{BE} - V_{TE} + V_{BE2} + e_2 \right\} \left(\frac{R_{E2} - R_{E1}}{2R_{EE}} \right) \right]$$

From the Appendix part 2, the prototype circuit expression results are quoted as

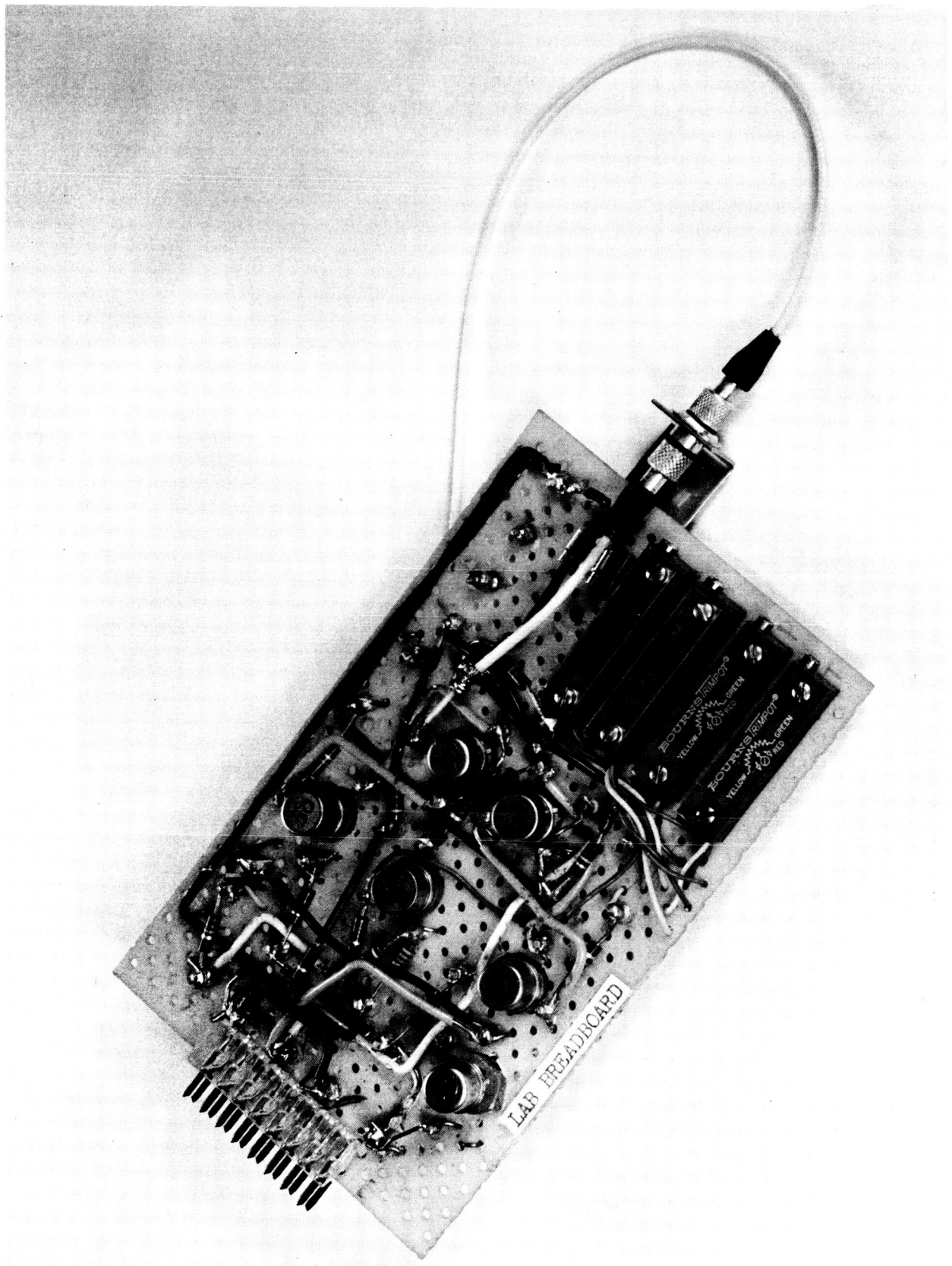


Figure 19. Breadboard Amplifier Design

$$e_o = 1 - \frac{R_{L1} + R_{L2}}{R} \left[(e_1' - e_1'') + (V_{BE1}' + V_{BE1}) - 1 \right]$$

It can quickly be seen that one of the major causes of instability has been eliminated. Also, a further improvement has recently been made available through the use of the 2N2060 differential amplifier input which gives more stability over a temperature range of -55°C to $+120^{\circ}\text{C}$. The maximum allowable differential variation of V_{BE} is 10μ volts $/^{\circ}\text{C}$ @ 0.1 ma.

6.3 Mechanical Development of a Breadboard Model

The problems involved in converting to a breadboard model have already received serious attention. To this end a breadboard model (figure 20) of the functional portions of the instrument was developed, fabricated, and assembled. The instrument can be satisfactorily converted to a breadboard model within the size and weight limitations, and it can be made to withstand the expected environmental extremes.

The cell is the main functional part of the assembly. It is the part that is used for detection of oxygen. The reservoir holds the electrolyte to prevent loss during sterilization and contains the electrolyte until it is ready for use. The injection valve prevents passage of the electrolyte until time for its use and allows the electrolyte to be delivered to the cell by breaking a frangible diaphragm. The accumulator allows space for gas expansion when the equipment leaves atmospheric pressure and furnishes space for excess electrolyte to prevent abnormally high pressures from developing in the system. This equalization also prevents pressure from interfering with oxygen infusion to the cell (figure 21).

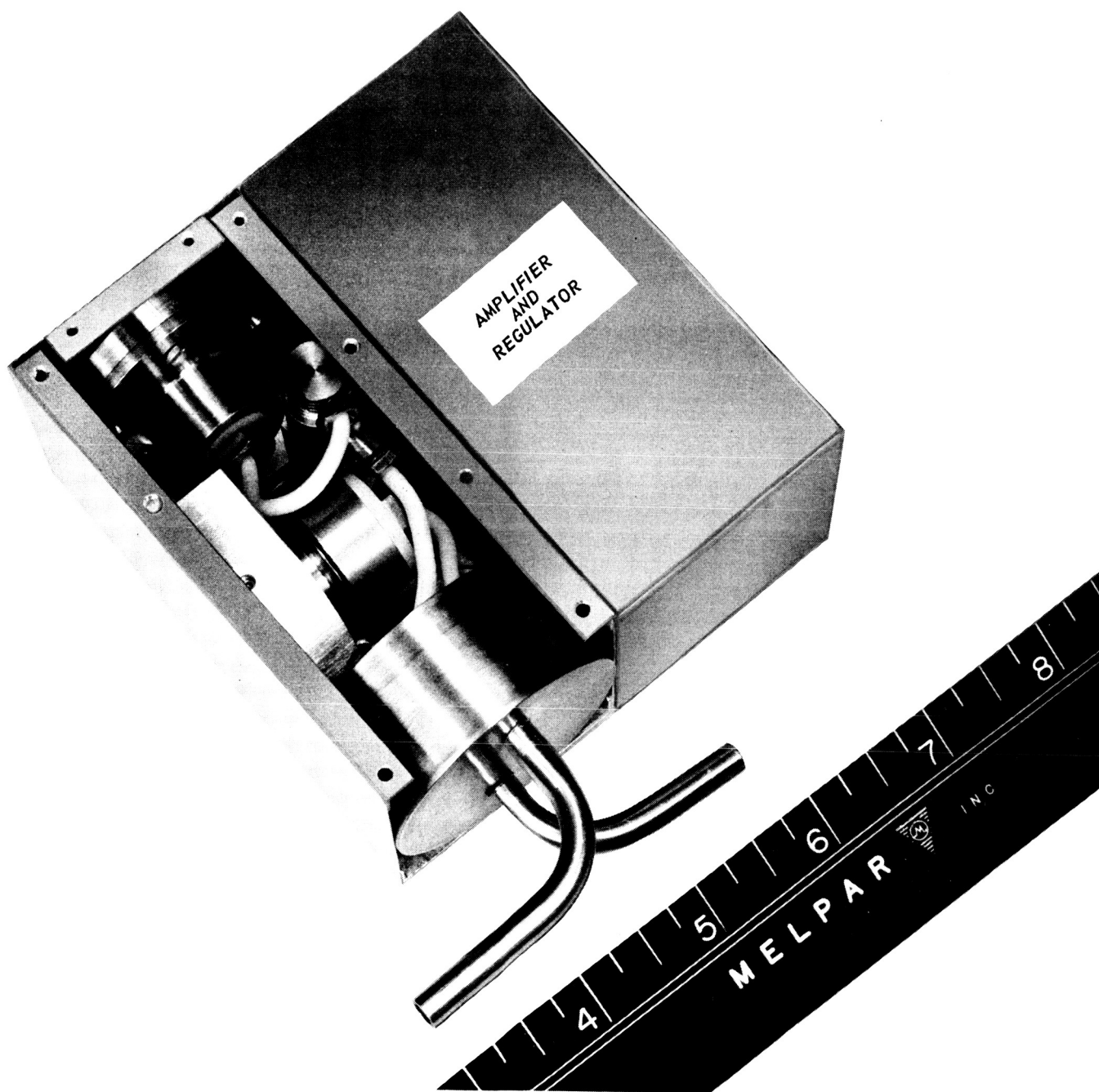


Figure 20. Breadboard Mockup

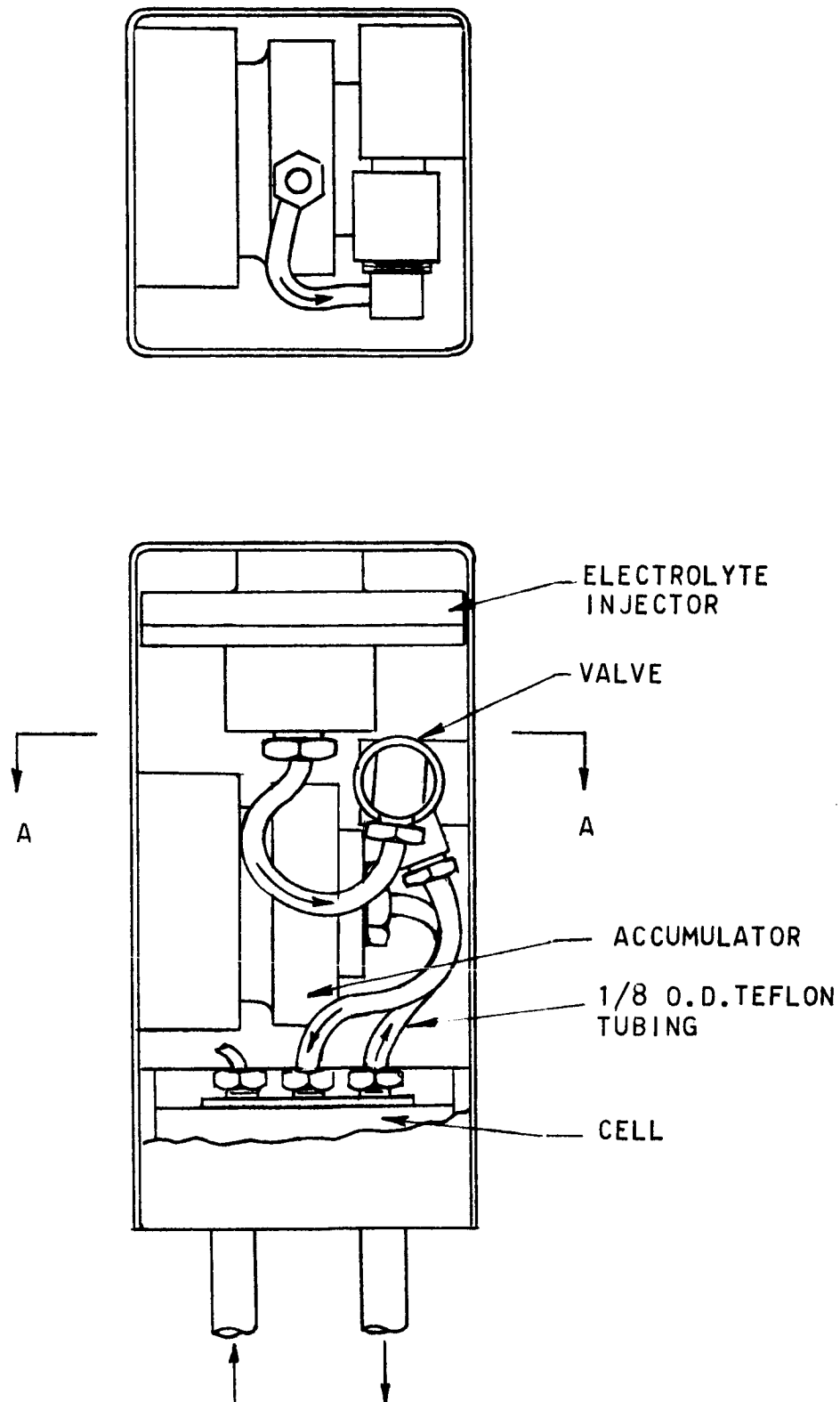


Figure 21. Air Sampling Unit

The cell (figures 22 and 23) consists of a Teflon diffusion membrane supported by a stainless steel screen, a combination platinum screen and foil cathode, a silicone rubber buffer washer, a Teflon mount washer, shim washers, a silver-silver chloride anode, an electrolyte delivery tube, a mounting ring and ring nut, and two external parts of the cell top and bottom, a gas diffusion plate and an O ring (figures 24 and 25). The Teflon diffusion membrane is supported by a stainless steel screen on the atmosphere side to prevent pressure differential inside the cell from separating the membrane and cathode or breaking the membrane. The cathode consists of a platinum screen and a platinum foil with the cathode electrical lead wire spot welded between the foil and screen. This provides a large cathode area and insures that there will be space for electrolyte entry. The platinum foil is fastened to a silicone rubber buffer which places a resilient member between the cathode mounting and the cathode and to prevent undue pressure from being exerted on the membrane by injection of the electrolyte between cathode and membrane. A silicone rubber adhesive was used to prevent contamination and give a good bond to the silicone rubber.

The silicone rubber buffer is fastened to a Teflon washer which gives a rigid mount to hold the cathode assembly in place.

The silver chloride-silver anode is located between the Teflon washer and the top of the cell. It is a wire that has been treated to give it a silver chloride coating. This wire is wound in a pancake coil for maximum area. Small Teflon washers are used between the anode wire and the Teflon washer to give the proper spacing between the membrane and the cathode screen. The washer thickness is adjusted as required to just allow the cathode screen to touch the membrane.

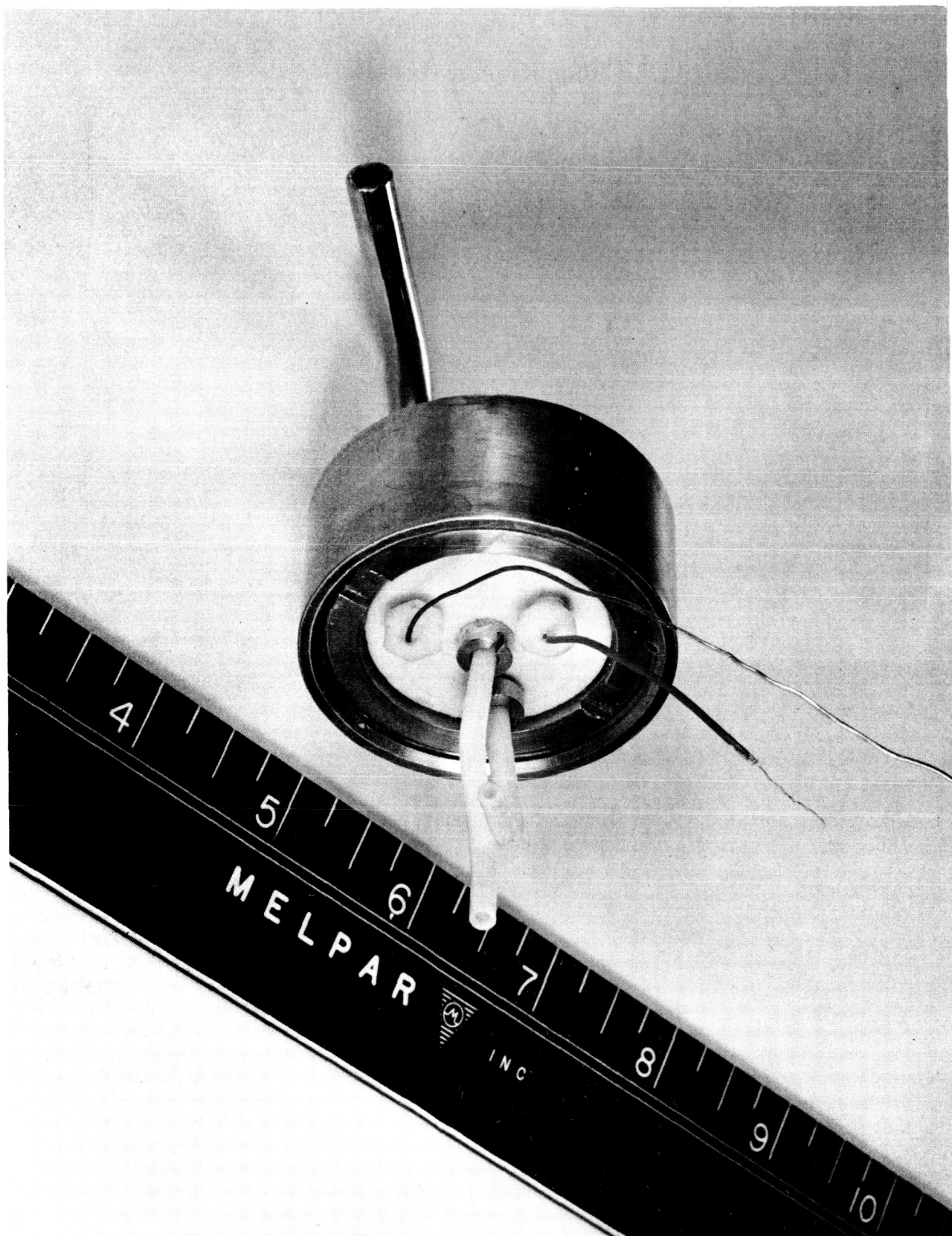


Figure 22. Breadboard Polarographic Cell

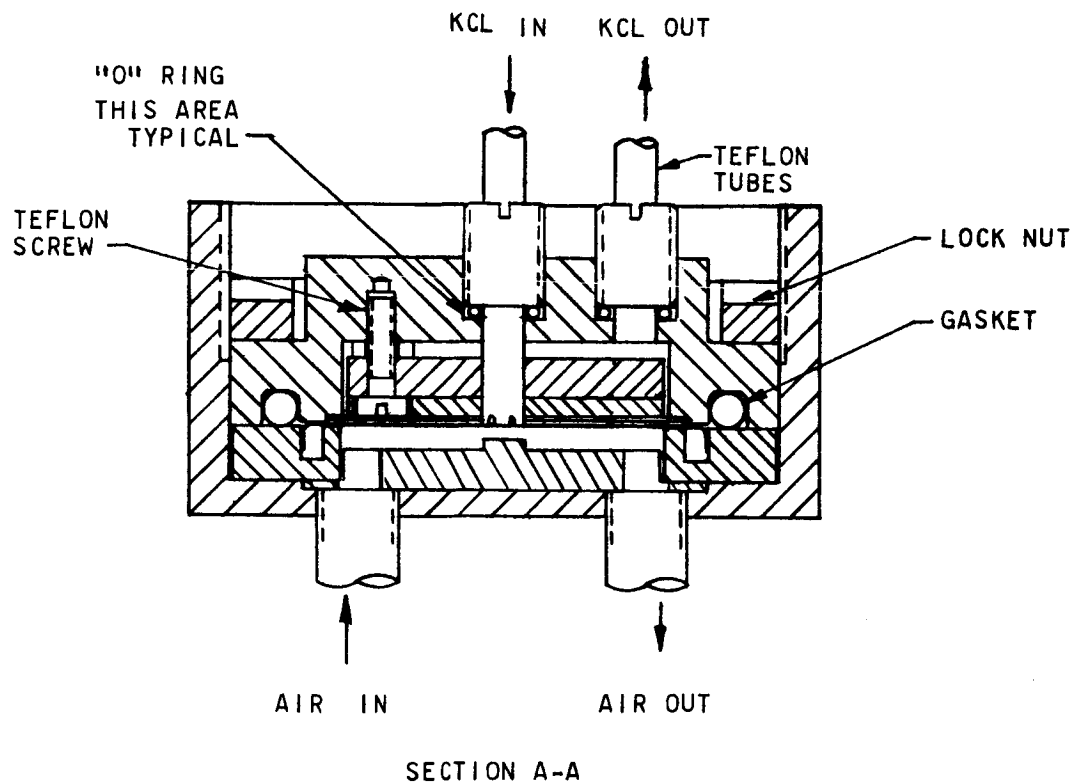
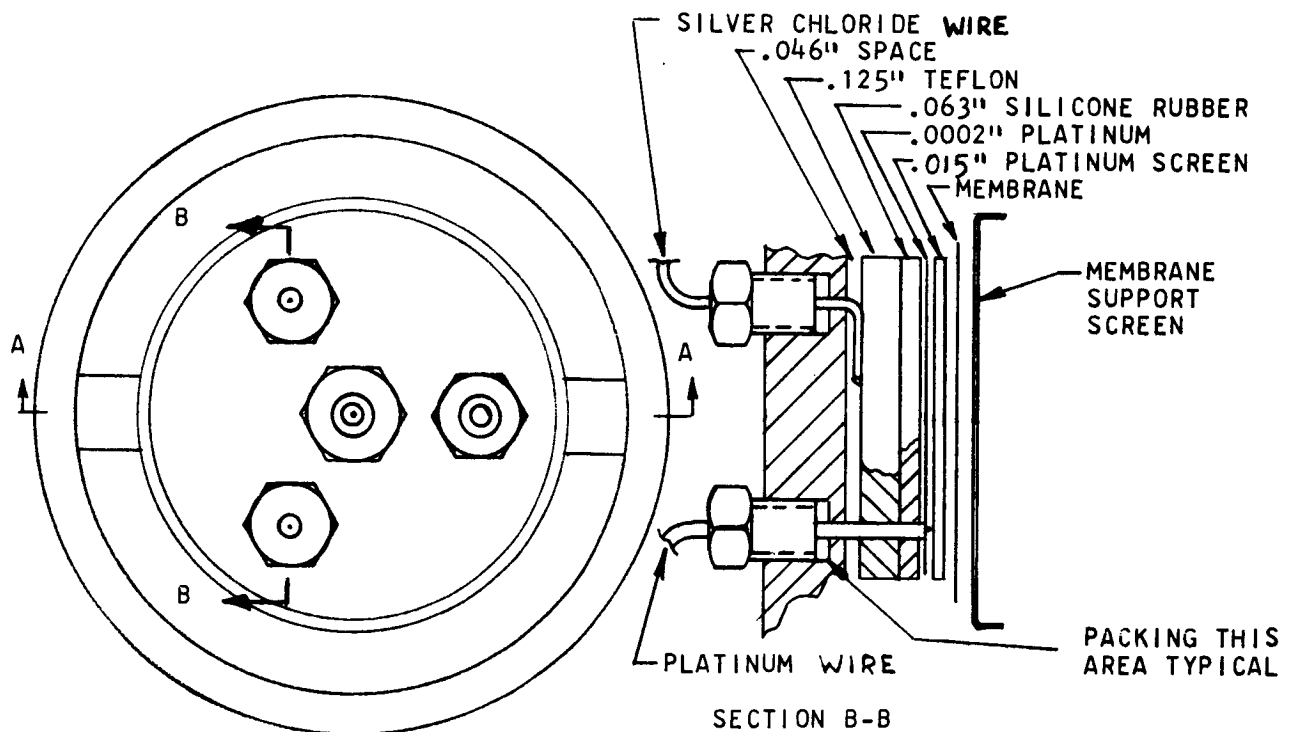


Figure 23. Breadboard Polarographic Cell

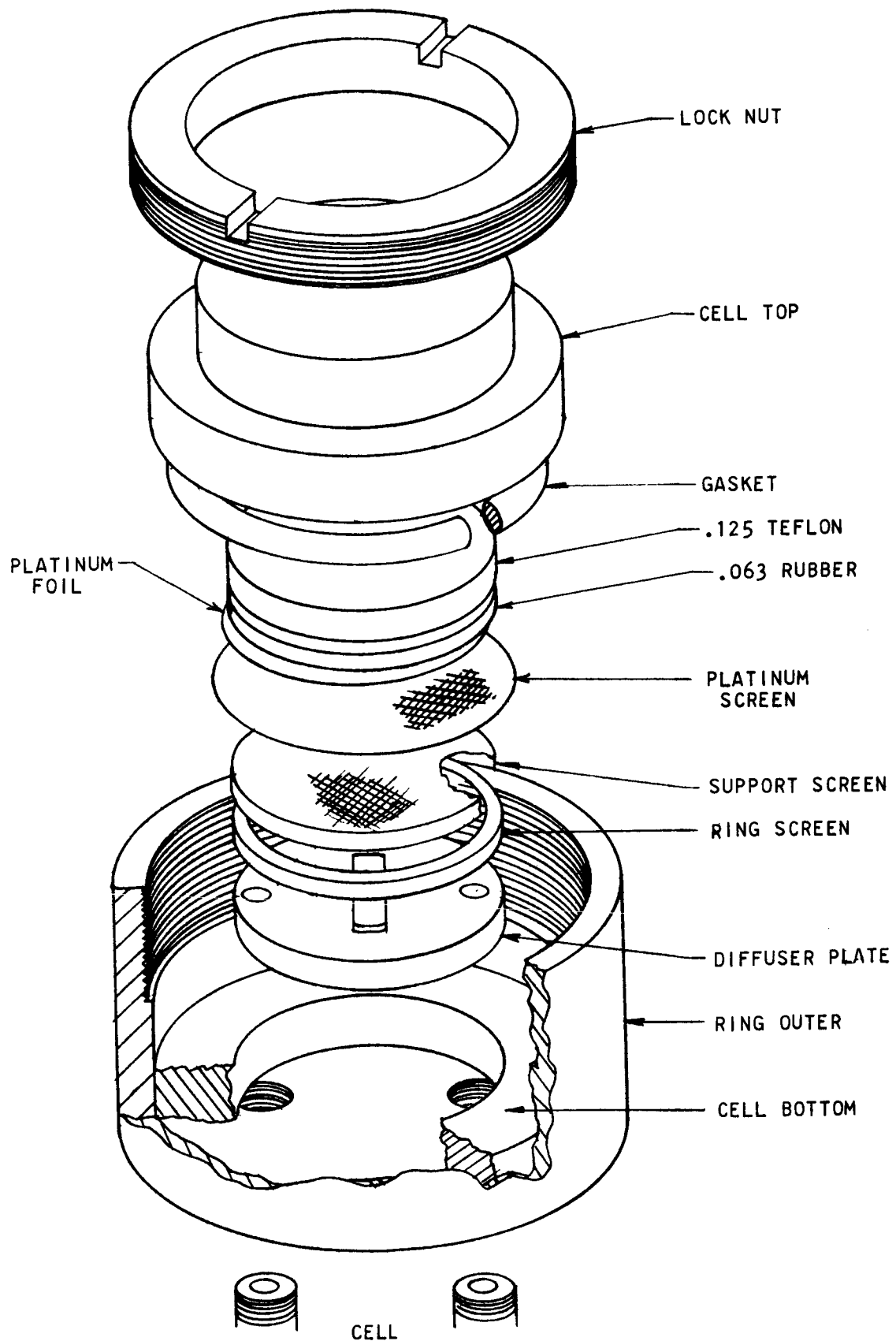


Figure 24. Cell-Exploded View

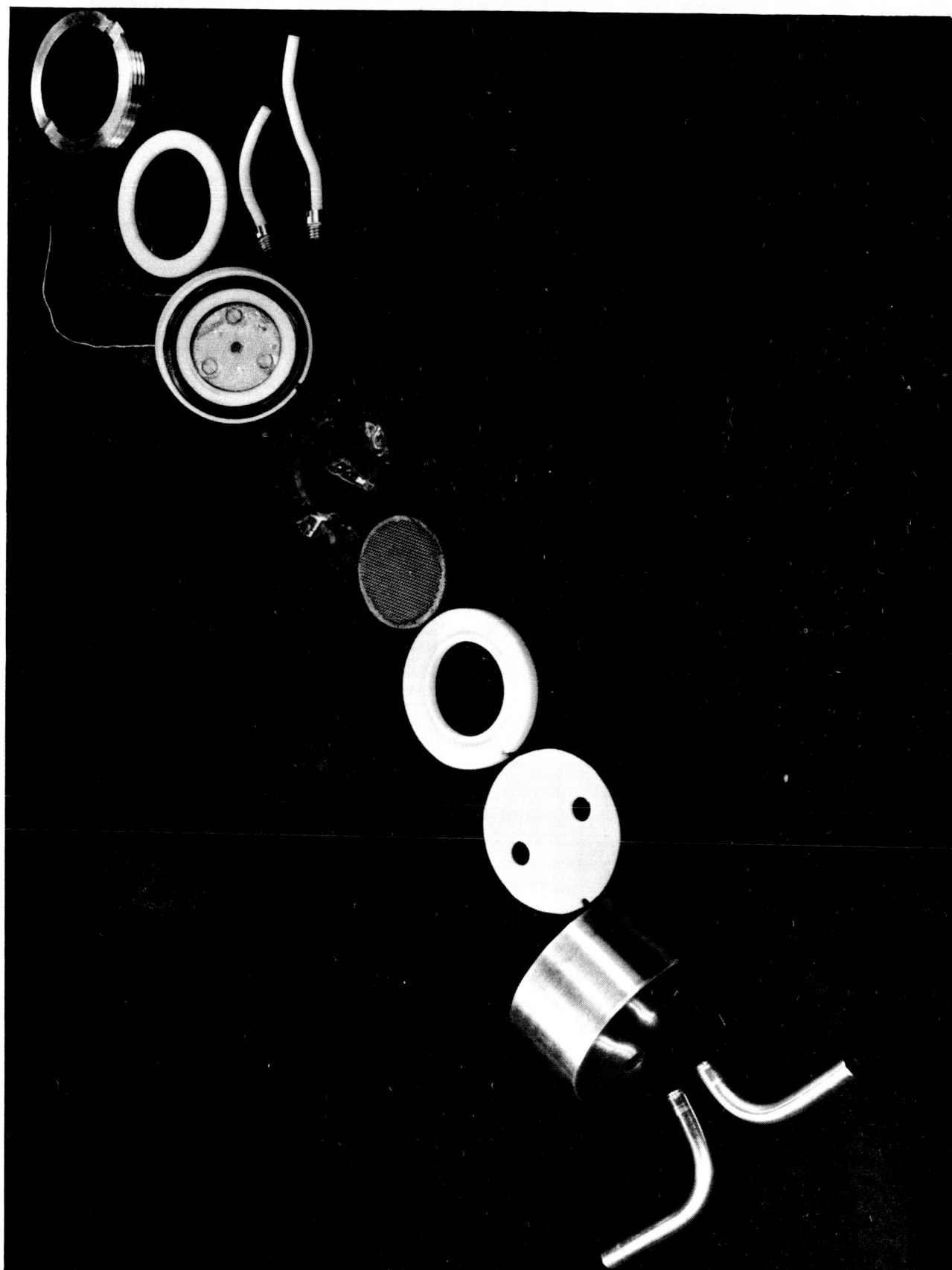


Figure 25. Cell-Exploded View

The electrolyte delivery tube is a Teflon tube that is closed on one end. It has six radial holes close to the closed end (figure 26). This tube passes through the top of the cell, the Teflon washer, the silicone rubber buffer and the cathode foil. The closed end rests against the top of the platinum screen. The closed end prevents electrolyte injection pressure from rupturing or deforming the Teflon membrane and the radial holes allow the injection of the electrolyte directly into the cathode area. This tube is held in place and sealed in the top of the cell by use of a gland screw against an "O" ring.

The cathode lead wire is platinum and the anode lead wire is silver to prevent any dissimilar connection actively from influencing the results. They are sealed in the top of the cell by use of gland screws.

The cell is held together by stainless steel cup-like ring with internal threads and a ring nut. The inlet and outlet gas tubes are fastened in the bottom of this ring.

The Martian atmosphere gas being tested comes in at one side of the membrane through the tube fastened in the outside ring, flows between the membrane and a diffuser plate and leaves through a tube fastened through the outside ring at the other side of the membrane. It has a central bar that tends to spread the gas entirely over the membrane area.

The electrolyte is sealed inside the cell by pressing the membrane against the bottom of the cell with an "O" ring.

The electrolyte injector (figure 27) consists of a rolling diaphragm piston, buffer washer, upper housing, lower housing and Teflon

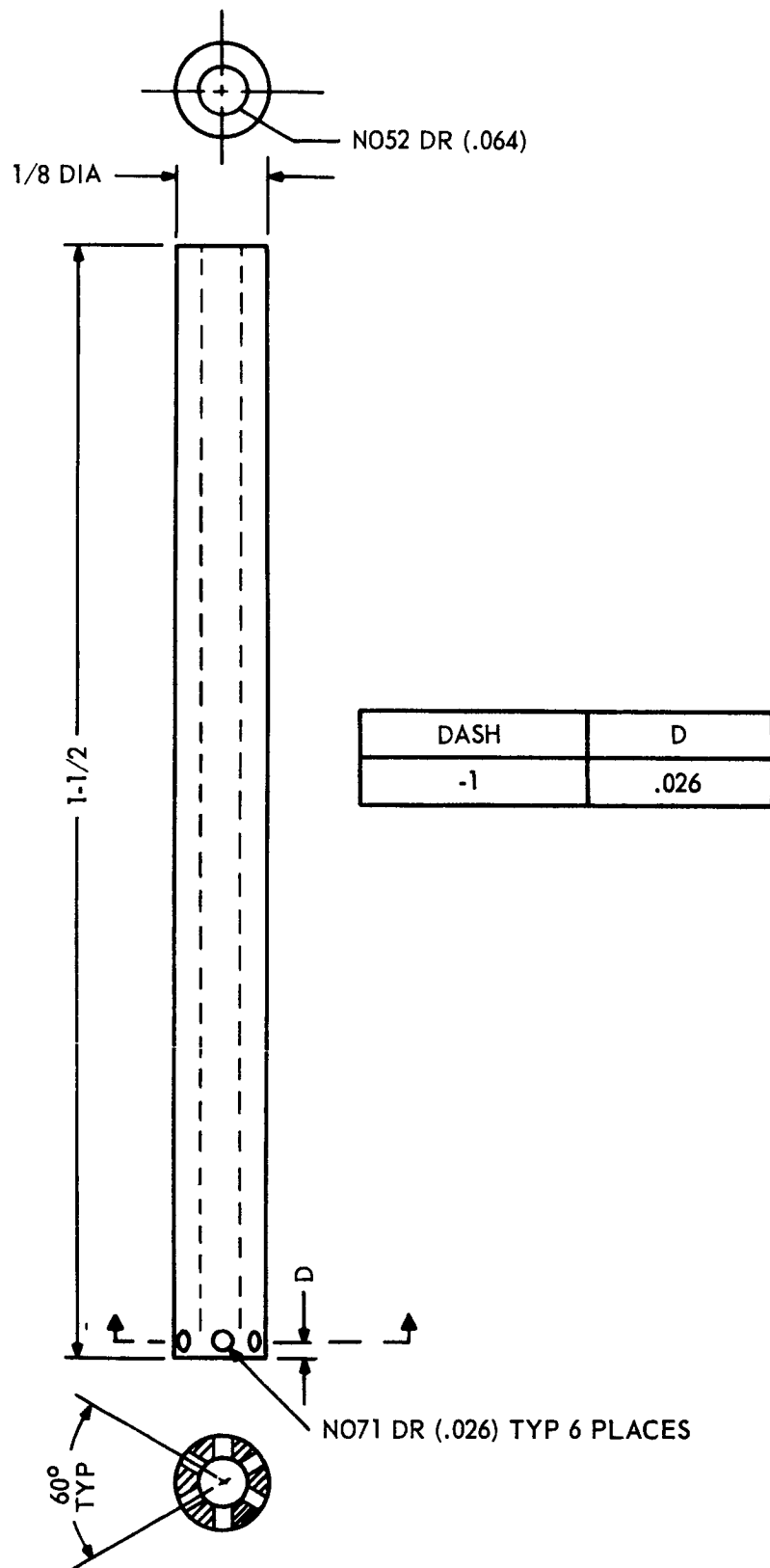


Figure 26. Electrolyte Delivery Tube

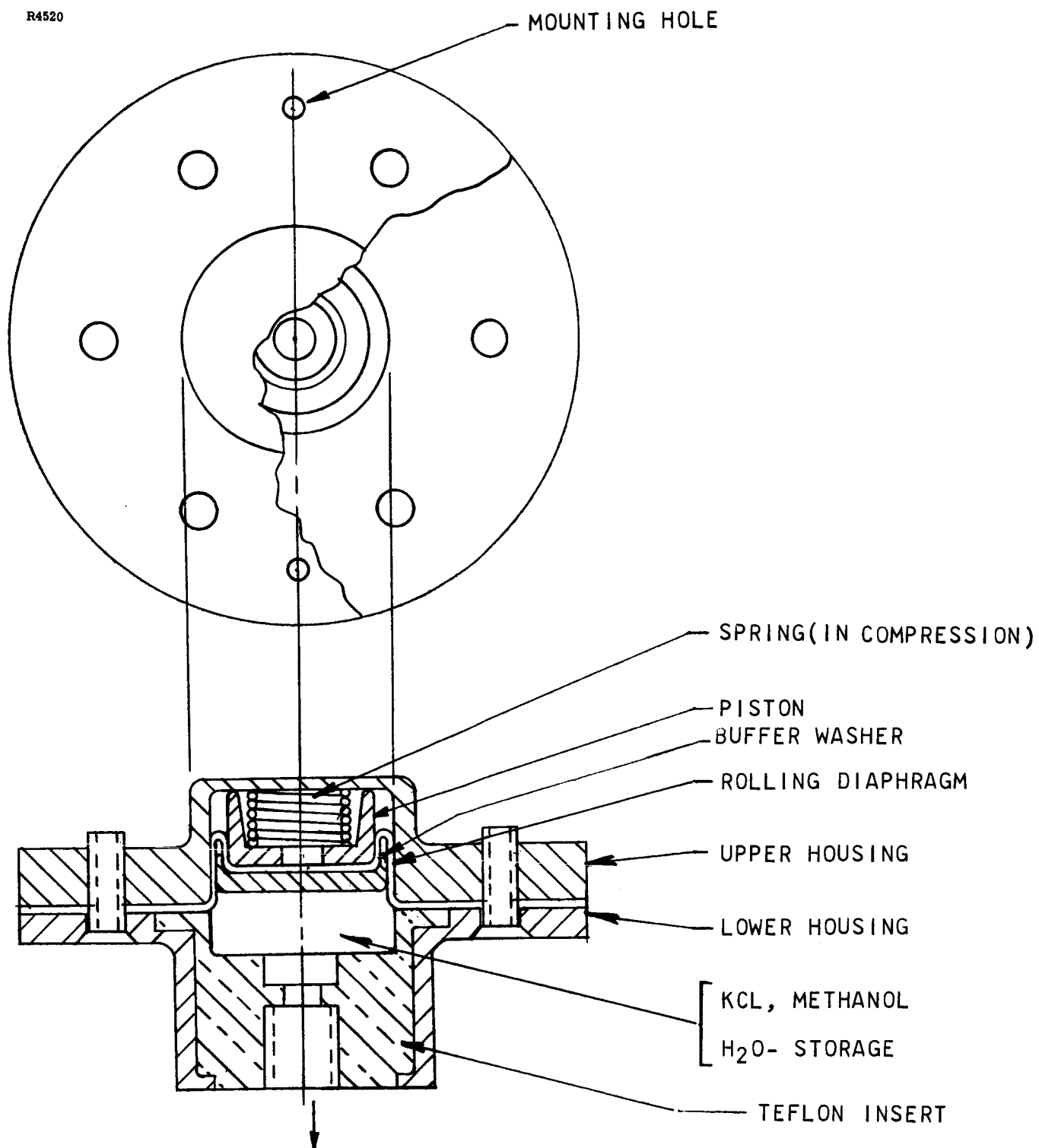


Figure 27. Electrolyte Injector

insert. Six screws pass through the lower housing and diaphragm edge and screw into the upper housing to hold the assembly together. Two holes are tapped into the top of the upper housing for mounting purposes.

The electrolyte is held in the electrolyte injector during sterilization to prevent loss due to evaporation. It is under a constant spring pressure of 15 pounds per square inch. When the injector valve opens the pressure forces the electrolyte into the cell for use. All parts in contact with the electrolyte are inert to it. The materials used in the crude breadboard were Teflon and synthetic rubber.

The rolling diaphragm retains the electrolyte in the lower chamber and allows some expansion space when the electrolyte freezes.

The piston retains the spring against side movement and distributes the spring pressure evenly over the diaphragm area.

The buffer washer maintains the rolling diaphragm shape and acts as a stop at the end of the injection stroke to protect the diaphragm from damage. It also functions as a sealing member for the screws that hold the piston diaphragm and spring assembly together.

The spring exerts a constant pressure on the diaphragm to force out the electrolyte when the injection valve opens.

The Teflon insert furnishes an inert material to be in contact with the electrolyte to eliminate contamination or corrosion. The upper and lower housing hold the assembly together and give a rigid surface to seal the diaphragm.

The injection valve consists of a Teflon lined plug, Teflon spacer, glass diaphragm, Teflon squib sleeve, stainless steel drive pin, explosive squib and housing (figure 28).

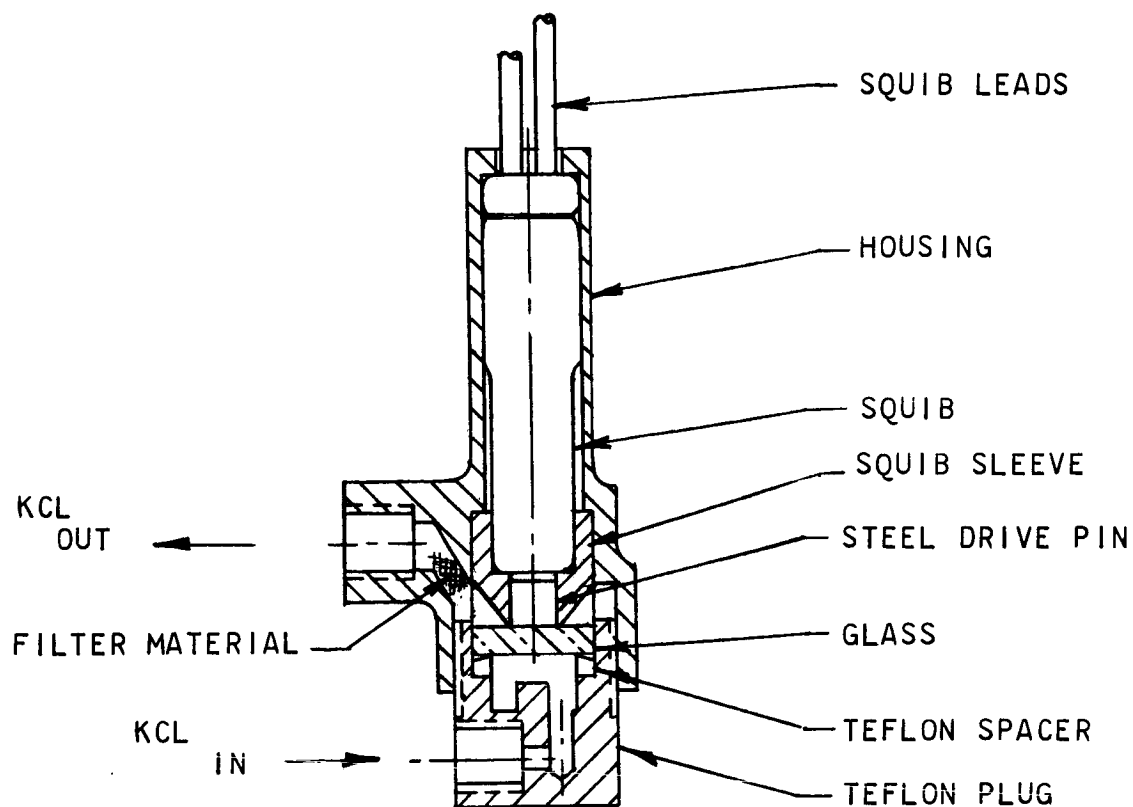


Figure 28. Valve

The Teflon lined plug seals the electrolyte in the injector by exerting pressure against the glass diaphragm through the Teflon spacer. It has threads that engage the housing to hold the entire assembly together. The plug contains a stop to keep the squib from traveling too far and introducing combustion gases into the system. The recesses in the bottom provide a place to hold fragments of the glass diaphragm after it has been broken.

The squib sleeve presses from the top down against the glass diaphragm to make a seal. Its material, Teflon, keeps the electrolyte from coming in contact with the brass squib materials. This prevents any corrosion, or contamination of the electrolyte.

The stainless steel drive pin also prevents the brass of the squib from coming in contact with the electrolyte. This pin is driven down into the glass diaphragm by the movement of the squib plunger which is driven by the explosion inside the squib.

The glass wool filter material at the outlet port prevents fractured material from being carried into the electrolyte distribution system.

The housing holds the assembly together and holds the explosive squib down against its explosive force.

When an electrical pulse is applied to the squib leads, the explosive powder inside the squib is ignited. The expansion of gases inside the squib forces a plunger against the steel drive pin. The steel drive pin breaks the glass seal which opens a passage between the electrolyte injector and the cell. The opening of this passage permits the pressure inside the injector to force electrolyte into the cell.

The accumulator is a device that equalizes pressure within the system. This device allows for expansion of the residual gas within the cell when low external pressures are encountered. This prevents abnormal pressures inside the system. An abnormal pressure inside the system might fracture or puncture the diffusion membrane. Internal pressure would interfere with the process of diffusion. The accumulator also furnishes an overflow space for any excess electrolyte and internal gas displaced by the electrolyte when it is injected into the cell.

The accumulator consists of a rolling diaphragm assembled in collapsed condition, an end plate, a case and a ring nut. The collapsed side of the diaphragm is connected to a port in the cell and the other side of the diaphragm is open to the external atmosphere. (See figure 29).

The rolling diaphragm functions as a bladder to make room for gas expansion and receipt of any excess electrolyte. The pressure of the ring nut seals the bladder and rim between the end plate and the case.

The case provides the expansion room in which the diaphragm can operate. The case top is vented to the exterior atmosphere. This part is made from non-magnetic stainless steel.

The end plate is made of Teflon to prevent a metal from coming in contact with the electrolyte. Contact of electrolyte and a metal during cell use may affect the function of the cell. This part is connected to the cell by a Teflon tube.

All interconnecting tubing is 1/8 inch outside diameter heavy wall Teflon tubing and all metallic parts are made with non-magnetic stainless steel.

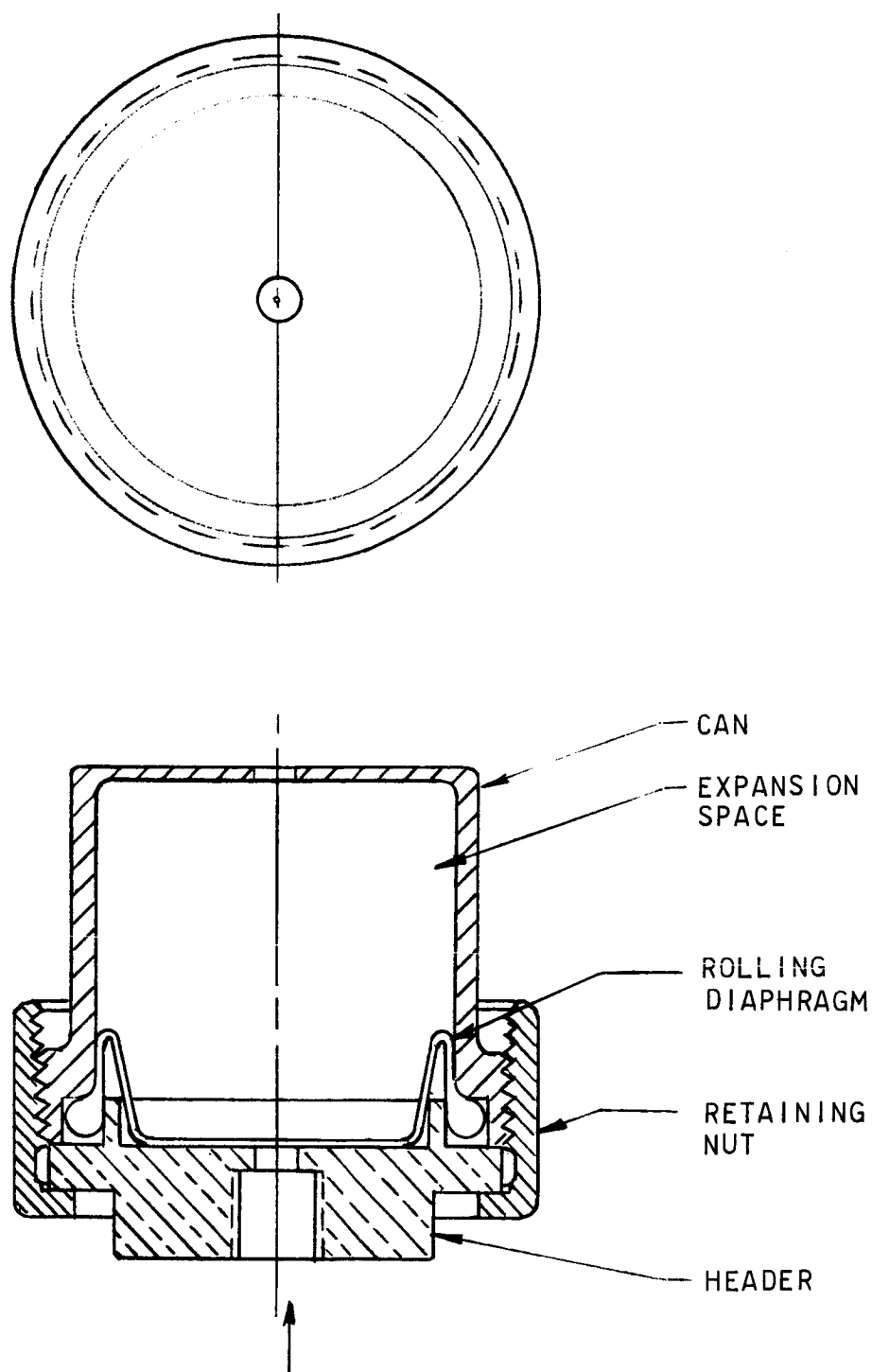


Figure 29. Accumulator

Consideration was given to the problem of insuring sample gas flow across the face of the cell in the instrument. While it is anticipated that ram air flow will assure this flow during descent, it is conceivable that sampling after impact will be desirable.

To this end a means of circulating sample atmosphere gas without the use of a motor driven device or other magnetic material components has been devised (figure 30). It consists of a small high pressure tank of gas, a miniature pressure regulator and a combination critical orifice Venturi tube. The gas from the pressure tank is delivered at a constant pressure to the critical orifice which is designed as a nozzle directed at the throat of the Venturi tube. As long as the manifold pressure remains below approximately half of the upstream pressure in the orifice, the flow from the orifice will remain constant.

Preliminary laboratory tests were made to determine the feasibility of this approach. It was found that a four to one gain can be realized for the manifold flow to the impelling gas.

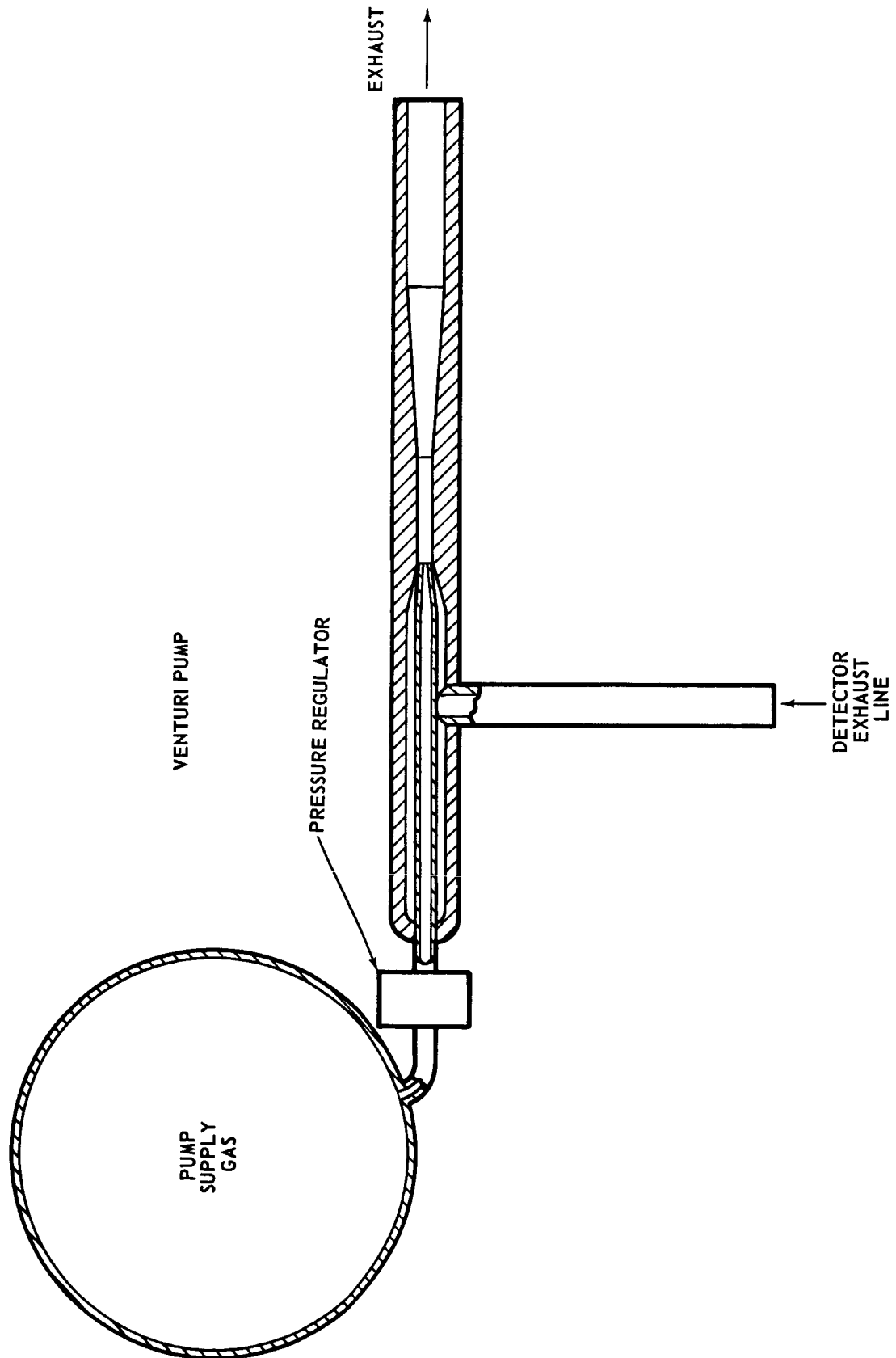


Figure 30. Venturi Pump

7. PROPOSED FUTURE EFFORT

A good deal of effort has already been expended, which will be directly applicable to the task of building a prototype model of the polarographic oxygen electrode. The first cut breadboard model already constructed, although not thoroughly tested, will provide a great deal of information with respect to building a prototype model capable of meeting requirements of all the specifications.

In the next phase of the work the electrochemical contribution will be relatively small, since the principle of the polarographic oxygen detector has been reduced to practice within the framework of the required specifications. The electronics and mechanical tasks will require greater effort in order to conform to the required specifications in the respective areas. Future effort for the three major parts are discussed below.

7.1 The Electrochemical Cell

There are only two significant changes that would appear desirable as far as the electrochemical aspects of the cell are concerned, and they affect the membrane and the electrolyte.

The membrane study should only involve a consideration of the feasibility of using silicone rubber. This membrane material has given some indications of being satisfactory, and the literature suggests that it should be promising. Very few thin silicone rubber membranes are commercially available. It will probably be necessary to have special silicone rubber membranes made up especially for this program.

It would be desirable to improve the electrolyte-solvent mixture from the standpoint of yielding higher diffusion currents, and working at the

extremely low temperatures. The electrolyte being used presently has a relatively low salt concentration because of the methanolic solution. Higher conductivity could be achieved with quaternary ammonium salts, or lithium chloride in various solvents such as acetonitrile, dimethylformamide and other well known electrochemical solvents.

7.2 Amplifier and Power Supply

Beyond the scope of the contract the breadboard amplifier, of section 6.2 was designed, developed, and integrated with the breadboard cell. Future recommendations leading to prototype development will be covered in this section. The cell reference supply, generally a secondary consideration, will also be covered in this section.

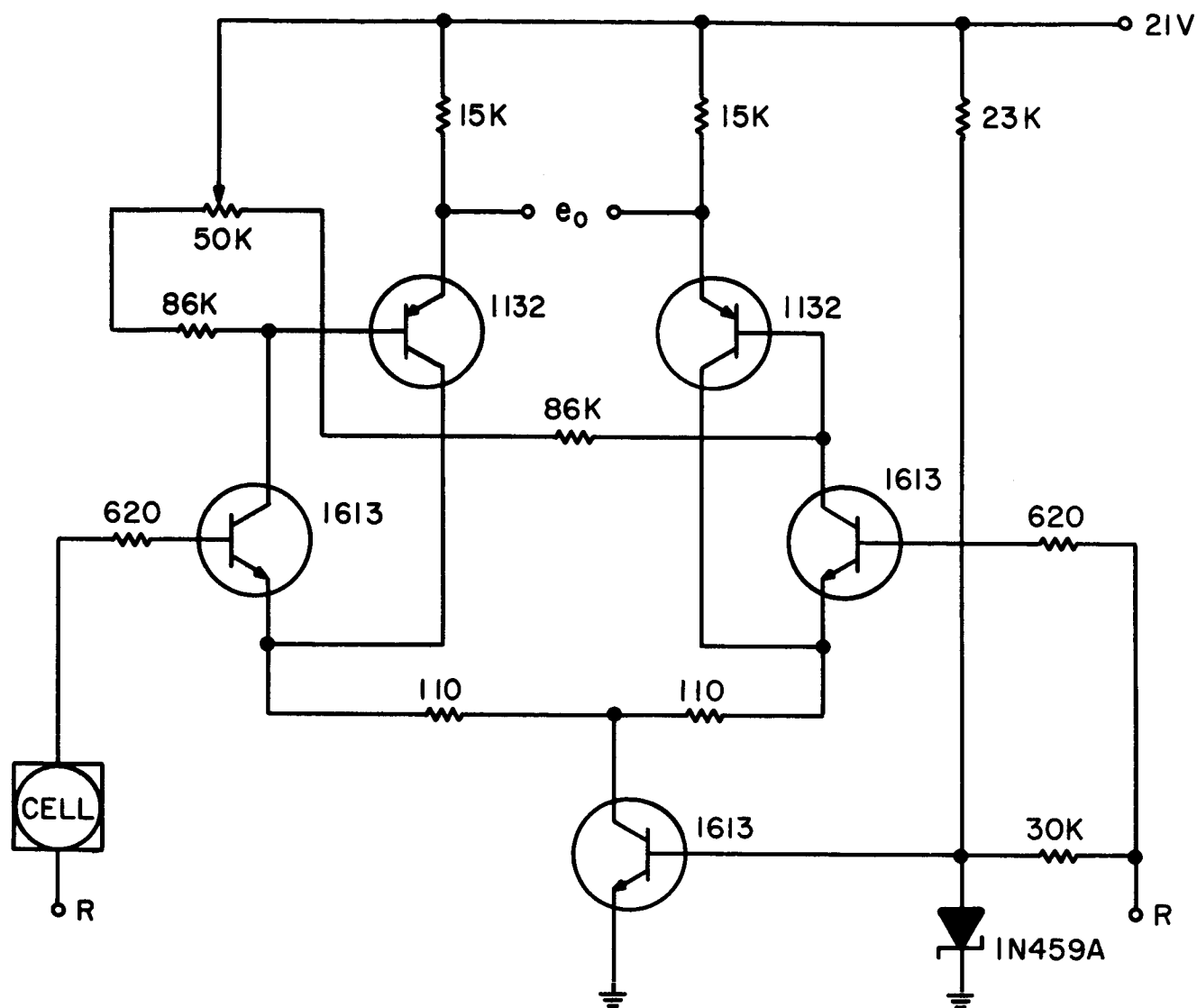
7.2.1 Amplifier

The designed and developed breadboard amplifier (see Figure 31a) has the necessary stability and drift rate to warrant very little more major considerations. Stability of better than $36 \mu\text{V}/^{\circ}\text{C}$ from 25°C to 125°C have been achieved. Power consumption for the prototype is rated at 100 milliwatts at 25°C .

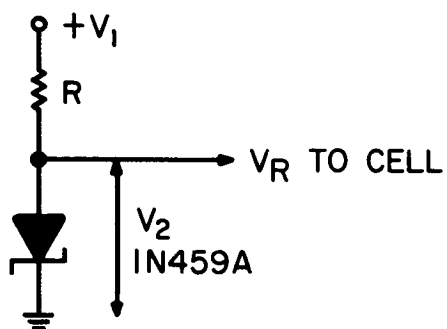
The recommendations for the future amplifier effort are:

1. Examine the possibility of using the 2N 2060 at the input stage on the prototype amplifier.
2. Adapt the prototype amplifier output to a single ended mode.
3. Using circuit topology, maximize the space considerations.
4. Begin the final component evaluation on the individual basis.

The recommendation of examining the 2N 2060 as an input stage possibility should seriously be considered. No circuit adaption would be



(a) BREADBOARD AMPLIFIER



(b) REGULATOR

Figure 31. Breadboard Amplifier and Regulator

required since the 2N 2060 is an electronic equivalent of the 2N 1613. The advantage lies in two factors. The 2N 2060 would essentially locate both the present 2N 1613's on the same transistor wafer improving the static thermodynamic consideration. The second factor is that better dynamic thermal tracking would be available, namely $10 \mu \text{ volts}/^{\circ}\text{C}$ from -55°C to 125°C at 0.1 mA. The second recommendation of single-ending the output is necessary for proper telemetering purposes. This may be accomplished as in the prior amplifier through the use of a single 2N 1613 and a voltage divider, with a 5K load resistor.

The third recommendation is essentially a miniaturization procedure designed to make optimum use of packaging the electronics system.

The component procurement and evaluation procedure would follow the specification code as outlined in the Appendix of JPL No. 20061A. The Melpar Minuteman reliability program, if necessary, may be implemented upon JPL's recommendation or retained on a consultation basis on any questionable items.

7.2.2 Power Supply

The cell reference supply design and development is straightforward. A Zener regulator is recommended from the standpoint of reliability and simplicity. A IN459A was experimentally found to be satisfactory using a 27K dropping resistor arrived at by the following calculation. This arrangement is shown in Figure 31b.

$$V_1 = 28 \text{ v}$$

$$\text{IN459A at 1 ma } V_2 = 0.64$$

$$V_R = V_1 - V_2 = V_1 - 0.64$$

$$V_R = 28 - 0.64 = 27.36 \text{ v}$$

$$V_R = I_R R$$

$$I_R = I_Z = 1 \text{ ma}$$

$$R = \frac{27.36}{1 \times 10^{-3}} = 27.36\text{K}$$

If unforeseen power considerations dictate use of a less consumptive regulator a transistor series type regulator would be adaptable, if the necessary safeguards are taken.

7.3 Projected Modification to Develop a Sophisticated Breadboard and Prototype

It is evident at the conclusion of this phase of development, that satisfactory oxygen detector breadboards and prototypes can be produced to meet the requirements set forth by the Jet Propulsion Laboratory. Modest modifications and extension of the design approach for a breadboard, previously described in section 6.3 would be required.

A compact unit including the cell, electrolyte injector, accumulator and electronic circuits has been visualized and is illustrated in figure 32. The cell is placed in a position to accommodate the placement of the injector and accumulator on either side to reduce wasted space. Directly adjoining this section is the electronic amplifier and behind that is the control circuit.

The injector conceived for future design would utilize a gas squib generator in place of the spring in the present crude breadboard. This technique has been used previously at Melpar for injection of electrolyte into high power density batteries with successful and satisfactory results.

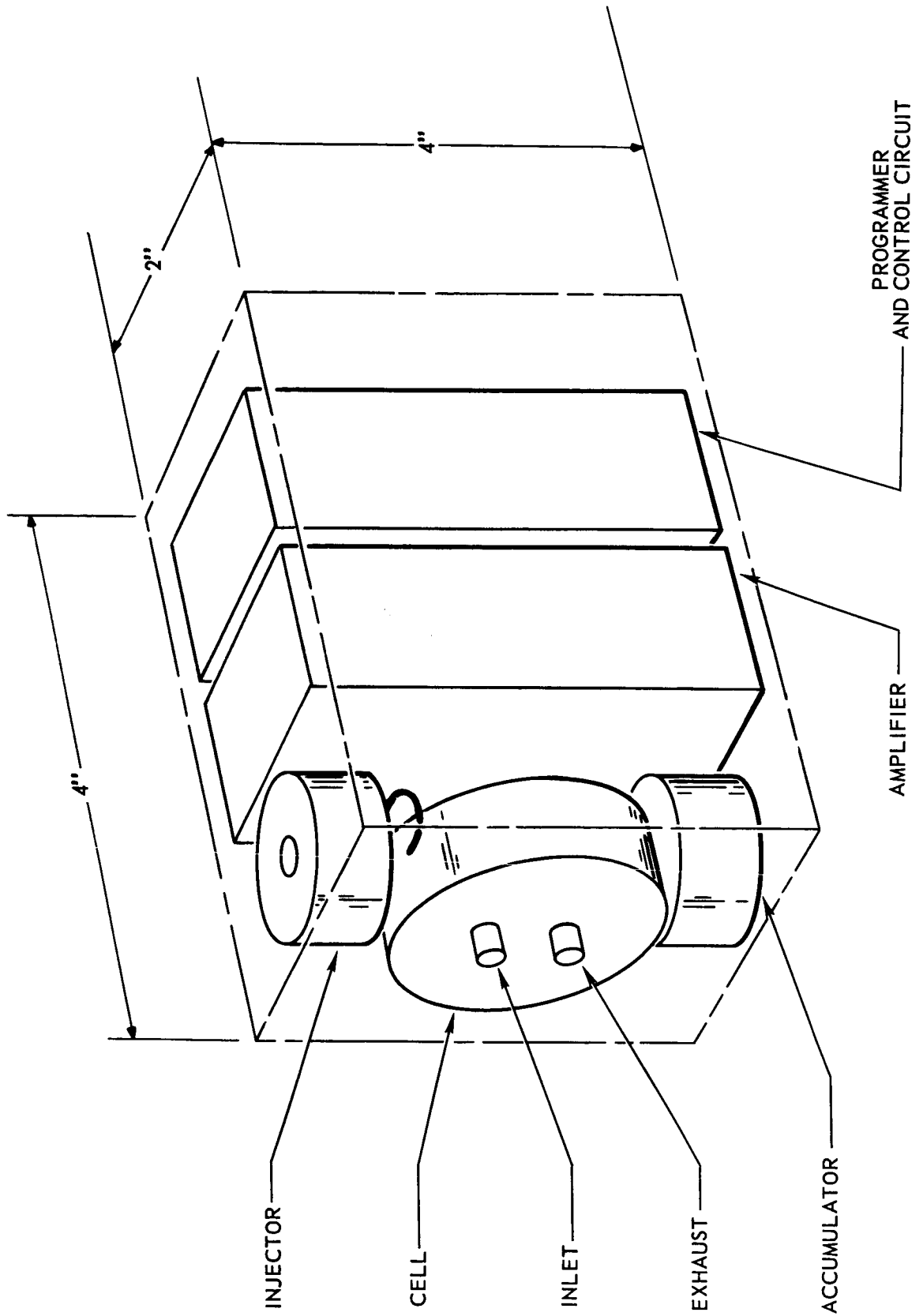


Figure 32. Proposed Compact Design

The squib actuator for releasing the electrolyte would work against a metal shear tip rather than a glass diaphragm to provide more rugged construction.

Transit sealing would be provided for the inlet and outlet gas sample ports in order to prevent deterioration of the cell during the long transit time. These seals would be opened in a manner similar to that used at the electrolyte injector.

Although stringent temperature control does not appear to be required for operation of the cell, it may be necessary to supply a small amount of heat to melt the electrolyte prior to operation. This is on the assumption that the electrolyte does solidify during transit. (In this connection it may be mentioned that the laboratory model has operated successfully at -25°C without heating.) This heating can easily be accomplished by the employment of a few judiciously placed thermite cells in the instrument. These thermite cells would be fired at a predetermined period of time prior to sampling and governed by the control circuit. Minimal insulation would be utilized to provide efficient heat transfer to the cell components without excessive heat loss.

Joining and sealing of the cell sub-assemblies would be accomplished by means of metal rollover and hermetic-sealing rather than threaded parts and "O" rings. Whereas non-magnetic stainless steel parts have been utilized in the breadboard design described above, many of these parts would be replaced with aluminum alloy sections to reduce weight.

The injector valve could be made as an integrated part of the electrolyte injector to further reduce the components needed.

Silicone rubber that will withstand very low temperatures should be used in any rolling diaphragm. Glass or metal fiber instead of organic fiber could be used as reinforcement.

A Teflon lined metal bellows or diaphragm could be substituted for the rubber diaphragm in the electrolyte injector to eliminate the possibility of low temperature fracture. Two or three explosive squibs would be used in each position to increase the reliability of action.

It is considered that the problem of the atmosphere sample movement past the instruments is common to other instruments used in the probe. For this reason the concept of a pressure tank supply and regulator working through a critical orifice venturi pump might best be considered as solving an overall Mariner probe manifold problem rather than an individual instrument problem. Further extension of this scheme as presented in section 6.3 may be developed by Melpar to provide air sample circulation for the entire probe.

Structural integrity of the electronic components in the instrument would be insured by mounting components in a formed housing, interconnecting of components by point-to-point wiring within this form, and finally complete encapsulation of the unit. This subassembly would then be mounted within the instrument by means of miniature non-bottoming isolators to minimize generation of microphonics and prevent damage due to shock and vibration.

It would be recommended that the complete unit be mounted firmly at least four points within the Mariner probe. This will allow effective bridge construction rather than cantilever construction with a resultant reliable unit.

8. APPENDIX

1. Amplifier Design Parameter Considerations

Highest current output from the cell

$$\begin{aligned} I_1 &= C_S \times G \times P \times t \\ &= 532 \times 10^{-6} \times \frac{1}{21} \times \frac{100}{760} \times 1 \end{aligned}$$

$$I_1 = 3.34 \times 10^{-6} \text{ Amperes}$$

C_S - Standard temperature, standard pressure,
air mixture cell current

G - Oxygen concentration variant

P - Pressure variant

t - Temperature correction factor

1 @ + 20°C ; 1/3 @ - 20°C experimentally determined

with platinum inlay electrode. Lowest current output from the cell

$$\begin{aligned} I_2 &= C_S \times G \times P \times t \\ &= 532 \times 10^{-6} \times \frac{1}{21 \times 10^3} \times \frac{10}{760} \times \frac{1}{3} \end{aligned}$$

$$I_2 = 1.11 \times 10^{-10} \text{ Amperes}$$

Cell impedance calculations

$$I(R) = V \quad \text{assume 0.70 volts RMS working voltage}$$

$$I_1(R_1) = V_1$$

$$3.34 \times 10^{-6}(R_1) = 0.70$$

$$R_1 = 212 \times 10^3 \text{ OHMS}$$

$$I_2(R_2) = V_2$$

$$1.11 \times 10^{-10} (R_2) = 0.70$$

$$R_2 = 6,360 \times 10^6 \text{ OHMS}$$

2. Circuit Analysis of the two regenerative pairs

The least involved method of analysis is to first examine one pair. (See figure 33)

I_{B1} is the base current of T_1 and the base current of T_2 is $h_{FE1} I_{B1}$. The collector current of T_2 it follows is $h_{FE1} h_{FE2} I_{B1}$.

$$I_{EE} = (1 + h_{FE1} I_{B1}) + h_{FE1} h_{FE2} I_{B1} \simeq h_{FE1} h_{FE2} I_{B1}$$

assuming leakage currents to be remissible

$$e'_1 - V_{B1} = I_{B1} R_{S1}$$

$$I_{B1} = \frac{e'_1 - V_{B1}}{R_{S1}}$$

$$V_{B1} = V_{BE1} + V_{E1}$$

$$= V_{BE1} - h_{FE1} h_{FE2} I_{B1} R_{EE} - V_{EE}$$

$$I_{B1} = \frac{e'_1 - V_{BE1} - V_{EE}}{R_{S1} + h_{FE1} h_{FE2} R_{EE}}$$

Considering e_o :

$$e_{o1} = V_{cc} - I_{E2} R_{L1}$$

$$I_{E2} = h_{FE1} h_{FE2} I_{B1}$$

$$e_{o1} = V_{cc} - R_{L1} h_{FE1} h_{FE2} \left[\frac{e'_1 - V_{BE1} - V_{EE}}{R_{S1} + h_{FE1} h_{FE2} R_{EE}} \right]$$

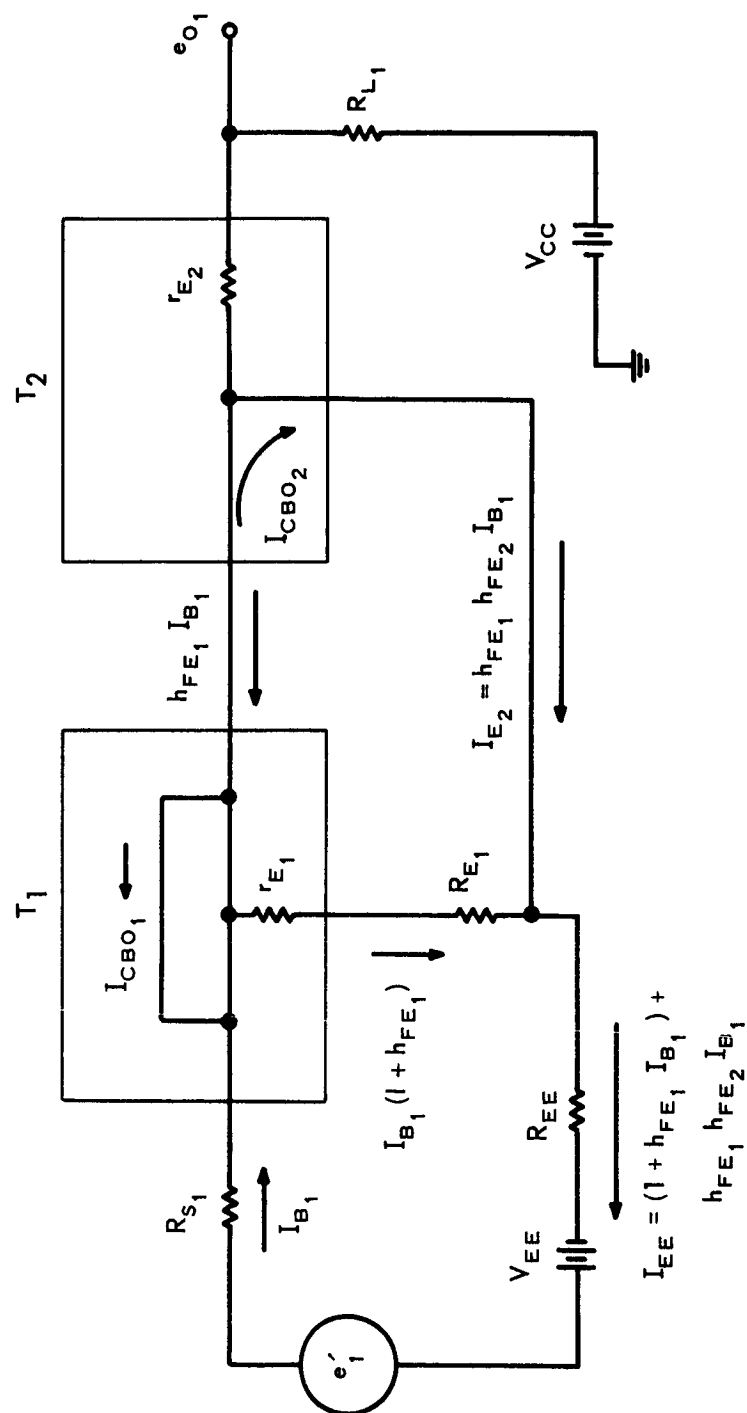


Figure 33. Circuit Analysis

$$e_{o1} \simeq V_{cc} - \frac{R_{L1}}{R_{EE}} \left[e'_{11} - V_{BE1} - V_{EE} \right]$$

where

$$(1 + h_{FE2}) \simeq h_{FE2}$$

and

$$R_{S1} \ll h_{FE1} h_{FE2} R_{EE}$$

and

$$R_{EE} \gg r_{E1} + R_{E1}$$

and

$$e_{o1} = V_{cc} - I_{E2} (R_{L1}) - I_{E2} r_{E2} \simeq V_{cc} - I_{E2} (R_{L1}).$$

By an equivalent analysis

$$e_{o2} \simeq V_{cc} - \frac{R_{L2}}{R_{EE}} \left[e'_{11} - V_{BE1} - V_{EE} \right]$$

therefore

$$e_{o1} - e_{o2} = 1 + \frac{R_{L1} + R_{L2}}{R_{EE}} \left[(e'_{11} - e'_{11}) + (V_{BE1} - V_{BE1}') + 1 \right]$$

or

$$\Delta e_o = - \frac{R_{L1} + R_{L2}}{R_{EE}} \left[\Delta e_1 + \Delta V_{VE} \right]$$

9. BIBLIOGRAPHY

1. Barrer, R. M., Diffusion In and Through Solids, Cambridge University Press, 1941.
2. Jost, W., Diffusion in Solids, Liquids, Gases, Academic Press, 1960.
3. "Standard Method for Gas Transmission Rate of Plastic Sheeting," ASTM Standards - 1958, Part IX, ASTM D 1431-58, p. 460.
4. Barton, R.S., "Permeability of Some Plastic Materials to Helium, Hydrogen, Nitrogen, Oxygen and Argon," Atomic Energy Research Establishment, Gt. Britain, M 599 (1960).
5. Brown, W.E., and Säuber, W.J., "Gas Transmission by Plastic Films," Modern Plastics 36, 107, (1959).
6. Stannett, V., Szwarc, M., Myers, A.W., "Evaluation of Gas Transmission Rates of Flexible Packaging Materials," U. S. Government Report, Research Department 31, 445 (1959). Final Report DA 19-129 QM 123 Quartermaster General, Quartermaster R + D U. S. Army, Natick, Mass.
7. Kammermeyer, K., "Silicone Rubber as a Selective Barrier," Industrial and Engineering Chemistry, 49, 1685 (1957).
8. Schrufer, B., "Semi-Micro Permeability Apparatus of Plastic Films According to Measurements of Changes in Pressure and Volume," Kunststoffe, 46, 132 (1956).
9. Membrane Phenomena Discussions, Faraday Society, Vol. 21 (1956).
10. "Theoretical Investigation of the Mechanism of Transfer of Materials Through Polyethylene," PB 121, 194 Aug. (1955).
11. Waak, Alex, Fritz, Stennet V., and Swarc, M., "Permeability of Polymer Films to Gases and Vapors," Industrial and Engineering Chemistry, 47, 2524 (1955).
12. Othmer and Frohlich, "Correlating Permeability Constants of Gases Through Plastic Membranes," Industrial and Engineering Chemistry 47, 1034 (1955).
13. Stannet, V., and Szwarc, M., "Permeability of Polymer Films to Gases - A Simple Relationship," J. Polymer Science, 16, 89 (1955).
14. Kirshenbaum, Steng and Dunlap, "Permeability of Different Elastomers to CO₂ Using C¹⁴," Rubber Age, 74, 903 (1954).
15. Brubaker, D.W. and Kammermeyer, K., "Separation of Gases by Plastic Membranes," Industrial and Engineering Chemistry, 46, 733 (1954).

16. Brubaker, D.W. and Kammermeyer, K., "Apparatus for Measuring Gas Permeability of Sheet Materials," Analytical Chem. 25, 424 (1953).
17. Norton, F.J., "Diffusion of Gases Through Solids," General Electric Review, 55, 28 (1952).
18. Smirl, V.L. and Hershberger, A., "Permeability of Polymeric Films to Gases," Modern Plastics, 27, 95 (1950).
19. Smirl, V.L., and Hershberger, A., "Permeability of Polymeric Films to Organic Vapors," Modern Plastics, 27, 97 (1950).
20. Reimouth, W.H., Advances in Analytical Chemistry and Instrumentation, Interscience, 1960, Vol. 1.
21. Sawyer, D.T., Pessok, R.L., and Jensen, K.K., "Polarograph with Direct Recording of Electrode Potential," Analytical Chemistry, 30, 481 (1958).
22. Laitinen, H.A., and Kohltoff, I.M., "Voltammetry with Stationary Microelectrodes of Platinum Wire," J. Phys. Chem., 45, 1061 (1941).
23. Laitinen, H.A. and Kolthoff, I.M., "Voltammetry Determinations and Amperometric Titrations with a Rotating Microelectrode of Platinum," J. Phys. Chem. 45, 1079 (1941).
24. Lingane, J.J., "Chronopotentiometric Study of Oxygen Reduction at a Platinum Wire Cathode," J. Electroanalytical Chem. 2, 296 (1961).
25. Anson, F.C., "Effect of Surface Oxidation on the Voltametric Behavior of Platinum Electrodes," J. Am. Chem. Soc. 81, 1554, (1959).
26. Anson, F.C., and Lingane, J.J., "Anodic Chronopotentiometry with Platinum and Gold Electrodes," J. Am. Chem. Soc. 79, 1015 (1957).
27. Kolthoff, I.M. and Tanaka, N., "Rotated and Stationary Platinum Wire Electrodes," Analytical Chemistry, 26, 632 (1954).
28. Laitinen, H.A., and Enke, C.G., "The Electrolytic Formation and Dissolution of Oxide Films on Platinum," J. Electrochem. Soc., 107,
29. Sawyer, D.T., Interrante, L.V., "Electrochemistry of Dissolved Gases - Reduction of Oxygen at Platinum, Palladium, Nickel and Other Metal Electrodes," J. Electroanalytical Chem., 2, 310 (1961).
30. Bagotski, V.S. and Motov, D.L., "Reversible Oxygen Electrode Based on Mercury in Alkali Solutions and the Mechanism of Cathodic Reduction of Oxygen," - Translation by Kushinoff, B.W., Applied Physics Laboratory, Johns Hopkins Univ., Library Bulletin, T6 230-T318, 24 July 1962.

31. Kovacs and Piroška, "Adjustment of Platinum Electrodes Used for Measuring Oxygen Tensions," - Naturwissenschaften 45, 285 (1958).
32. Krog and Johanson, "Teflon Covered Platinum Microelectrode," Review Scientific Instruments, 30, 108 (1959).
33. Rayment, R.B., "Temperature Effect on the Polarographic Oxygen Electrode," Anal. Chem., 34, 1089 (1962).
34. Orritt, D.E., and Kanwisher, J.W., "An Electrode System for Measuring Dissolved Oxygen," Anal. Chem. 31, 5 (1959).
35. Sawyer, D.T., George, R.S. and Rhodes, R.C., "Polarography of Gases - Quantitative Studies of O_2 and SO_2 ," Anal. Chem. 31, 2 (1959).
36. Thayer, L.C. and Czuha, "Method of Oxygen Analysis," U.S. Patent 2,943,028.
37. Koyama, K., "Galvanic Cell For Determining Oxygen in Gases Containing CO_2 ," Anal. Chem. 32, 1053 (1960).
38. Wise, W.S., "Continuous Estimation of O_2 in Gases Using a Polarographic Method," Chem. and Ind. 17, 37 (1948).
39. Larcher, T.B., Czuha, M., "Automatic Recorder for Continuous Determination of O_2 in Gases Using the Dropping Mercury Electrode," Anal. Chem. 26, 1351 (1954).
40. Wright, Lindsay, "Dissolved Oxygen Analyzer," Proc. Am. Power Conf. 21, 706 (1959).
41. Hersch, P.H., "Trace Monitoring in Gases Using Galvanic Systems," Anal. Chem. 32, 1030 (1960).
42. Coetzee, J.F., Cunningham, G.P., McGuire, D.K., Padmanabhan, G.R., "Purification of Acetonitrile as a Solvent for Exact Measurements," Anal. Chem., 34, 1139 (1962).
43. Shilling, G.I., "Extreme Model Atmosphere of Mars," Rand Publication RM 2782 - JPL, June 22, 1961.
44. Kellogg and Sagan, "Atmospheres of Mars and Venus," Natl. Acad. of Sc, Publ 944.
45. Ozone Chemistry and Technology, American Chemical Society, Advances in Chemistry Series, No. 21.
46. Thorp, Bibliography of Ozone Technology, Armour Research Foundation, Vol. 1, Chicago, Ill. (1954).

47. Miller, B. "Instruments Evolve for Mariner Probes," Aviation Week and Space Tech, 76, 57 (1962).
48. Kolthoff, I.M. and Lingame, J.J., "Polarography," Interscience, 1952, Vols. 1 and 2.
49. Brezina, M. and Zuman, P., "Polarography in Medicine, Biochemistry and Pharmacy," Translated from the Czech by Wawzonek, S., Interscience, 1958.
50. Delahay, P., "New Instrumental Methods in Electrochemistry," Interscience, 1954.
51. Kolthoff, I.M., and Jordan, J., "Exaltation of the Limiting Current of Oxygen by Hydrogen Peroxide at the Rotated Gold Electrode as a Means for Amperometric Determination of Traces of O₂," Anal. Chem. 24, 1071 (1952).
52. Wall, R., "Development of a Trace Oxygen Analyzer," Ind and Eng Chem, 49, 77A (1957).
53. Roberts and Grinich, "The Annealing of Neutron Damage in Silicon Mesa Transistors," presented at IRE Wescon, August 1959.
54. Hilbiber, D.F., "A New D.C. Transistor Differential Amplifier," presented at Solid-State Circuits Conference Philadelphia, Feb. 1961.
55. Lauritzn and Leistiko, "Field Effects as Low-Noise Amplifiers," Fairchild Semiconductor, TP-19, February 1962.
56. DeMatteis and Halligan, "Designing Transistorized Differential Amplifiers," Electronic Design, 10, 16, 72 (1962).
57. Holladay, R., "Semiconductor Failure Analysis Using Characteristic Curves," Electro-Technology, 70, 2 (1961).
58. Praglin and Nichols, "High Speed Electrometers For Rocket and Satellite Experiments," IRE, 48, 4 (1960).
59. Beneteau, P.J., "The Design of High-Stability DC Amplifiers," Fairchild Semiconductor, APP-23/2.
60. Schwartz, Seymour, editor, Selected Semiconductor Circuits, NObsr 73231; Bureau of Ships, Dept. of the Navy.
61. Ludwig, G.H., "The Development of a Corpuscular Radiation Experiment for an Earth Satellite," Ph.D Dissertation, Dept. of Physics and Astronomy, State University of Iowa.

62. Middlebrook and Taylor, "Differential Amplifier with Regulator Achieves High Stability, Low Drift," Electronics, July 1961.
63. Slaughter, "The Transistor Emitter-Completed Amplifier," 1954 Wescon Proceedings.
64. Williams, Tarpley and Clark, "D.C. Amplifier Stabilized for Zero Gain," AIEE Transactions, 67, 47- 1948.
65. Goldberg, "Stabilization of Wideband D.C. Amplifiers for Zero and Gain," RCA Review, June 1950.
66. Hamlin, editor, "Fan Out No. 111 Minuteman Reliability of one Transistor," August 1962, Fairchild Publication.
67. We are indebted to Mr. Ellsworth Hughes of the Protective Development Division, CRDL, Edgewood Arsenal for suggesting the method for ozone production.

10. CONTRIBUTORS TO THE PROJECT

Contributions to the project were made by the following technical personnel:

Electrochemistry

Dr. R. T. Foley

Gerald Halpert

Bruno M. Vasta

Eric G. Back

Reginald W. Bours, III

John Peter Hoybach

Electronics and Instrumentation

Robert J. Janda

Mechanical Engineering

Philip J. McCabe

Andrew C. Madsen

11. PROGRAM SCHEDULE

Figure 34 is the program schedule followed during the period of this contract. It originates with the literature survey and includes all the subjects of experimental interest in the design of the polarographic oxygen detector. For the calibration of the laboratory model, descent tests were included. The instrumentation problems were also considered.

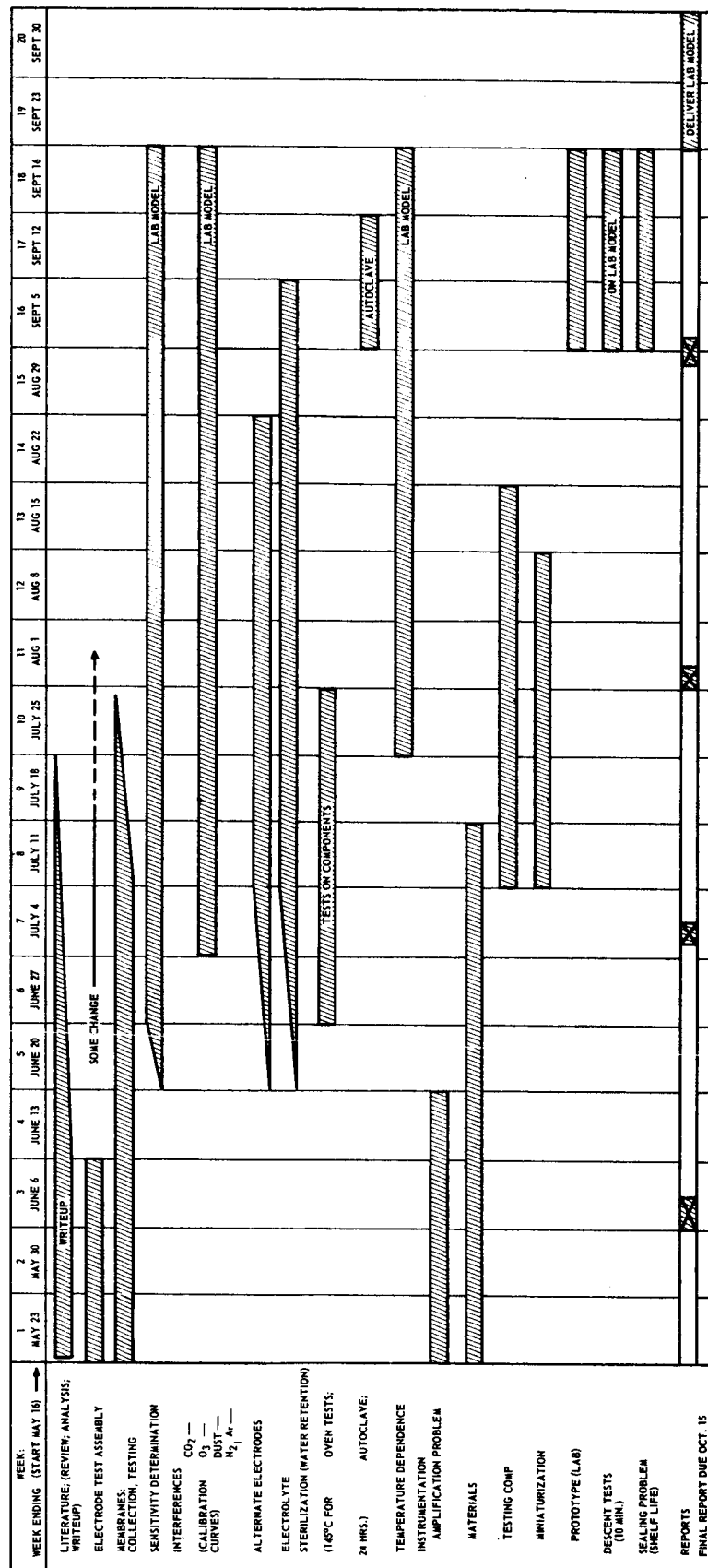

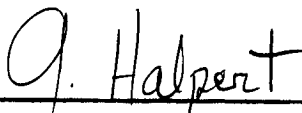
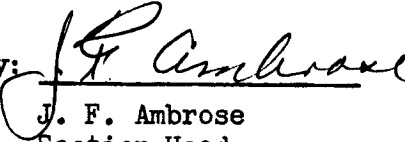
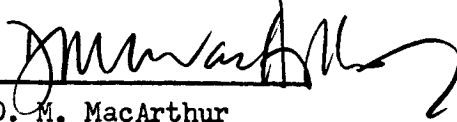



Figure 34. Program Schedule

Prepared by: 
R. T. Foley
Project Scientist


G. Halpert
Physical Chemist

Approved by: 
J. F. Ambrose
Section Head


D. M. MacArthur
Head,
Chemical and Life Sciences Department


P. E. Ritt
Vice President - Research